VOL. II. [JUNE, 1880.] NO. 3.

AMERICAN CHEMICAL JOURNAL.

CONTRIBUTIONS FROM THE SHEFFIELD LABORATORY OF YALE COLLEGE.

No. V.

ON THE DENSITY OF THE VAPORS OF SOME AMMONIUM AND AMMONIA COMPOUNDS.

BY W. G. MIXTER.

Ammonium Acetate.

Cahours* obtained acetamide in trying, by Dumas' method, to find the gas density of ammonium acetate. This salt, as is well known, yields on distillation ammonia, ammonium acetates, and finally acetamide. In the latter the nitrogen is not separated from the carbon by heat. This fact suggested the possibility of the existence of gaseous ammonium acetate at low temperatures and pressures. The results show dissociation analogous to that of ammonium chloride.

The experiments were made with a Hofmann apparatus with a calibrated thermometer hung between the walls of the eudiometer and the jacket tube. The graduations of the barometer and cathetometer used corresponded at common temperatures, and the latter admitted of readings to within $\frac{1}{2}$ mm. The weight of 1 c. c.

* Liebig's Ann. 128, 75.

of hydrogen was taken at 0.0000896 gram, and that of ammonia gas at 0.000762 gram. The coefficient of expansion used is 0.00366. The ordinary corrections were made for the expansion of mercury and the tension of its vapor. Experiments A were made with 0.060 gram of an ammonium sesquiacetate, which was made by passing ammonia gas into glacial acid and heating the product several hours in an air bath at 100°. Its composition was found by distilling with standard potash into standard acid and titrating both. The result was exactly three molecules of acetic acid to two of ammonia. Whether this composition was accidental was not determined. In the remaining experiments ammonia gas dried by potash was introduced into the eudiometer, and acetic acid was added in very nearly the amount required to form a neutral salt. The ammonia was measured at 100° in B and C, and at 185° in D and E. The acetic acid was purified by crystallization and melted at 15°, except that used in E which melted at 16°. According to Rüdorff,* acetic acid melting at 14.8° contains 0.99 per cent. of water.

	A		B			C		D	E
Weight of Acetic Acid.	..	..	..	0.0323	..	0.0388		0.2437	0.0485
Weight of Ammonia.	..	..	..	0.0096	..	0.0106		0.0691	0.0139
C. c. of Ammonia at 0° and 760 mm.	..	..	..	12.6	..	13.9		90.7	18.2
Temperature.	131.2	183.6	100.4	130.0	182.6	100.4	130.	184.6	185.
Pressure in mm.	274.8	314.4	81.0	101.8	118.5	82.7	120.4	552.6	345.6
Volume in c. c.	111.4	125.0	250.6	257.3	264.4	236.5	250.6	397.1	132.4
Density, H=1.	24.6	21.7	24.0	20.0	18.9	29.3	20.5	20.3	19.4
Pressure on Acetic Acid	148.5	187.1	28.8	47.	58.2	21.6	58.2	261.7	170.4
Density of Acetic Acid in Ammonia Gas.	38.3	30.5	52.3	33.5	29.8	88.4	33.3	33.4	30.6
Naumann's density of Acetic Acid, H=1.†	35.7	30.8	38.5	33.5	..	..	..	32.1	30.8
At pressure.	157.5	191.5	77.7	93.	..	..	..	269.	191.5
And temperature.	130.	185.	100.	130.	..	..	..	185.	185.

The theoretical density of a mixture of four volumes of ammonia and six volumes of acetic acid gas is 21.4, and that of two volumes of each gas is 19.25. It is evident if normal ammonium acetate splits into acetamide and water, or partially into these bodies and partly into ammonia and acetic acid, that the theoretical density of the mixed vapors would be 19.25. No acetamide or water was detected in the crystalline products remaining in the eudiometer

* Ber. deutsch. chem. Gesell. 3, 390. † Liebig's Ann. 155, 325.

after each experiment. The crystals were insoluble in ether and gave no odor of acetamide on gently warming. In view of the possibility that acetamide might be formed and then changed back to ammonium acetate, 0.0761 gram of pure acetamide was placed in the eudiometer. It was not all volatilized at 188.5° and a pressure of 266.8 mm. An equivalent of water was then added, and the whole did not evaporate at 185.5° and 523 mm., a pressure not as high as in experiment D. 0.021 gram of acetic acid was then introduced and the eudiometer kept some time at 185°. After cooling the tube was washed with ether. All the crystals dissolved, and the residue remaining after the evaporation had the odor of acetamide. In B, after successive heating to 100°, 130° and 182°, and cooling between each heating, a temperature of 100° was then applied. Before a second observation could be made, which would show whether the heating had been for a sufficient time, the tube broke. The density found was 25 or 1.1 higher than before found. The conclusion is that very little and probably no acetamide was formed in the experiments.

In the table are given Naumann's results on acetic acid, which were obtained under nearly similar conditions of temperature and pressure. His figures are reduced to the hydrogen standard, and correspond within errors of experiment to the densities found for acetic acid when mixed with ammonia gas, except the writer's results at 100°, which are questionable, owing to the uncertainty of complete evaporation. Acetic acid vapor and ammonia gas were slowly passed through thin tubes, a centimeter wide and a meter long, into a small tube holding a delicate thermometer whose bulb was between the two currents of gas. The small tube mentioned was surrounded by a thick jacket tube. The apparatus was heated to 186° by aniline vapor, and no change in temperature was observed, either when the gases met about the thermometer bulb or when the flow of the gases was stopped.

Ammonium Benzoate.

To 4.14 c. c. ammonia gas in the eudiometer was added 0.0285 gram of resublimed commercial benzoic acid, rather more than sufficient to form a normal salt. The observations made at 189° and a pressure of 134.5 mm. reduced to 0° and 760 mm. gave a volume of 8.8 c. c. The density of benzoic acid at 189° and 73.2 mm. in this experiment is 68.2. A direct determination made of

the same benzoic acid at the same temperature and a pressure of 119.2 mm. gave 69.3. The theoretical density of the acid is 61.1.

The following determinations were made by Victor Meyer's method. In place of the simple lead bath described by him,* a lead bath was used four inches in diameter holding an inch and a half gas pipe a foot long and closed at its lower end.† In this air-filled gas pipe was placed the evolution tube, and the top of the pipe was closed with two pieces of sheet copper. The lead bath was placed in a small firebrick-lined soldering stove, and was heated by one large Bunsen burner. The thinness of the glass of the evolution tube compelled the use of the air bath in place of a lead bath. A determination of the vapor density of mercury in the apparatus filled with air gave 100.1; theory 99.9.

$$2NH_3.SiF_4.$$

This compound was prepared by bringing dry silicon fluoride into an excess of dry ammonia. By distilling with potash and titrating 24.22 per cent. of ammonia were found; theory 24.58 per cent. The substance was introduced into the air-filled apparatus in a small platinum tube improvised of foil, which showed no residue after the experiments.

Substance.	c. c. gas at	temperature.	Barometer at 0°.	Density.
0.0331	17.3	23°	759.4	23.8
0.0311	16.5	19°	760.6	23.

A mixture of four volumes of ammonia and two volumes of silicon fluoride has a theoretical gas density of 23. H = 1.

$$NH_3.BF_3.$$

Boron fluoride was evolved from boric oxide, fluor spar and a large excess of oil of vitriol, and was passed into an excess of dry ammonia. The product was pink colored from one black rubber connector used. Ammonia found 20.39 per cent.; theory 19.94 per cent. The apparatus was filled with dry air.

Substance.	c. c. gas at	temperature.	Barometer at 0°.	Density.
0.0329	17.6	19.4°	754.8	23.
0.0322	17.4	20.8°	754.4	22.9

* Ber. deutsch. chem. Gesell. 1878, 2255.

† Since this paper went to press we have received Meier and Crafts' article (this Journal, 2, 108, and Ber. deutsch. chem. Gesell. 1880, 851), in which they describe a similar lead bath.

Another preparation was made with apparatus of only glass, and an excess of boron fluoride was used. The ammonia found was 19.91 per cent. The apparatus was filled with dry air.

Substance.	c. c. gas at	temperature.	Barometer at 0°.	Density.
0.033	17.7	22.6°	765.9	23.
0.0322	17.4	24.6°	765.9	23.1

The theoretical density of a mixture of two volumes of ammonia and two volumes of boron fluoride is 21.3 The temperature of the air bath was higher in the last two experiments, and was above the melting point of zinc. The ammonia boron fluoride melts and evaporates rapidly and leaves no residue when volatilized in platinum, but both the vapor and liquid attack glass slightly. In all the density determinations of the substance the glass showed a faint coating after washing with water, which explains the 1.7 excess found. It is possible that the action on glass was due to ammonium fluoride, but the ammonia estimation of the second preparation does not indicate it, nor was the long wide glass tube corroded through which the boron fluoride passed in the preparation of NH_3BF_3. The substance showed only a trace of silica when treated with water, and a little $2NH_3SiF_4$ would not affect the results. 0.2758 gram gained weight slowly in the air, and showed an increase of 0.008 gram in two days.

$$2NH_3.SnCl_4.$$

Tin tetrachloride, made by passing chlorine over hot tin, was freed from traces of moisture by distillation from oil of vitriol. It was poured into a dry bottle into which a rapid stream of ammonia was passing. The following is the analysis of the compound:

	Calculated.	Found.	
Sn	40.16	40.14	
Cl_4	48.24	47.78	
$2NH_3$	11.60	11.90	11.85

A portion of the substance exposed to the air a day gained eight per cent. in weight. The apparatus was filled with dry air, and the temperature was considerably above the fusing point of zinc.

Substance.	c. c. gas at	temperature.	Barometer at 0°.	Density.
0.0598	16.4	23°	750.9	46.
0.0706	19.8	23.4°	750.9	45.

The theoretical density corresponding to six volumes is 48.9.

In the following experiment the apparatus was filled with nitrogen which was freed from traces of oxygen by passing over glowing copper and copper oxide. It was dried by oil of vitriol on broken glass. A residue 0.0014 gram remained in the platinum tube after the experiment, and this was deducted from the weight of substance taken. The heat was the same as before.

Substance volatilized 0.0771, 22.3 c. c. at 29.4°. Bar. at 0° 760. Density, 44.5.

The glass was somewhat acted upon in each experiment with the tin compound, and an iridescence was marked. The substance volatilized too slowly at the melting point of lead and somewhat higher temperatures for a determination by Meyer's method.

Summary.

Ammonium acetates and ammonium benzoate dissociate completely into ammonia and the respective acids when heated under low pressures. $2NH_3.SiF_4$, NH_3BF_3 and $2NH_3.SnCl_4$ dissociate at temperatures above 300° into ammonia and the respective compounds of fluorine and chlorine. This may be easily shown by heating the ammonia compounds in a test tube and testing the reaction of the escaping vapors, which at first are alkaline and afterward acid.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

RESEARCHES ON THE SUBSTITUTED BENZYL COMPOUNDS.

No. IV.

PARACHLORBENZYL COMPOUNDS.*

By C. Loring Jackson and J. Fleming White.

In the third paper of this series the necessity of a revision of all the so-called parachlorbenzyl compounds was pointed out, and the results were described, which had been obtained from the investi-

* Proceedings American Academy of Arts and Sciences. Communicated by the Authors.

gation of some of them by Mr. A. W. Field and one of us. This work is now finished, and the present paper contains a description of the preparation and properties of the remaining parachlorbenzyl compounds, which have been heretofore made in an impure state, and also of a few related substances not as yet described.

Parachlorbenzylbromide, melting-point 48½° (made from pure paratoluidine), was used as the starting-point for these compounds, and therefore they cannot contain the isomeric impurities which caused the mistakes of our predecessors.

A comparison, in tabular form, of our more important results with the earlier ones, will be found at the end of the paper.

Parachlorbenzylsulphoacid, $C_6H_4ClCH_2SO_3H$.

This substance was first studied by Böhler,* whose paper, published in 1869, contains a description of the preparation of the potassium salt by heating chlorbenzylchloride with neutral potassic sulphite. It was, in fact, one of the papers coming from Strecker's laboratory to illustrate his general method of making sulphoacids,† first announced in 1868. The salt was thus obtained in colorless needles which gave with baric chloride glistening crystals of $(C_7H_6ClSO_3)_2Ba.H_2O$; the acid (made from the barium salt with sulphuric acid) formed when heated with an excess of plumbic hydrate, a basic lead salt, $(C_7H_6ClSO_3)_2Pb.PbO.H_2$, crystallized in scales with a silvery lustre; while with less plumbic hydrate a neutral salt was obtained, which, however, he did not analyze. All these salts were made from ordinary chlorbenzylchloride, and must therefore have been contaminated with the corresponding ortho compounds, as indeed was proved by Vogt and Henninger,‡ who took up the subject again in 1872, and by fusing the potassium salt (made according to Böhler's method) with potassic hydrate obtained a mixture of salicylic and paraoxybenzoic acids. They did not try, however, to separate the para from the ortho compound, but contented themselves with analyzing Böhler's potassium and barium salts: for the first they found the formula $C_7H_6ClSO_3K.H_2O$; it crystallized from water in concentric groups of large flat needles, from alcohol in pearly plates, lost its water of crystallization at 160°, and was decomposed at higher temperatures; their barium salt agreed in amount of water of crystallization and properties with

* Böhler, Ann. Chem. Pharm. 154, 56. † Strecker, Ann. Chem. Pharm. 148, 90.
‡ Vogt and Henninger, Ann. Chem. Pharm. 165, 372.

that of Böhler, except that it crystallized in bunches of needles. In preparing their potassium salt Vogt and Henninger observed the formation of an insoluble substance which, purified by crystallization from alcohol, melted at 167° and had the formula $(C_7H_6Cl)_2SO_2$; from the mother-liquors small quantities of two other substances were obtained, melting at 149° and 185°, and apparently having the same composition; they supposed, therefore, that the main product (melting-point 167°) was a mixture of these, and called it chlorinated benzylosulphide,—a name which, according to our present nomenclature, would be altered to dichlorbenzylsulphone. For a revision of their work on this substance, see page 167.

In taking up the subject we followed the method of our predecessors, except that we used sodic instead of potassic sulphite,* which we made by saturating one-half of a strong solution of sodic carbonate with sulphurous dioxide, and then adding to it the other half. After boiling this solution with parachlorbenzylbromide, in the proportion of one molecule of bromide to one of sulphite, in a flask with a return-cooler for seven hours, the smell of the benzylbromide had disappeared; the liquid was therefore allowed to cool, and the insoluble portion removed by filtration. This should have been the sulphone described by Vogt and Henninger, but it melted at about 55° instead of 167°, and a qualitative test showed that it contained no sulphur; from the smell it seemed to be an impure parachlorbenzylalcohol, formed by the action of the water on the bromide, and it was not thought worth while to investigate it farther. Although we have repeated the preparation of the sodium salt many times, we have never observed the formation of Vogt and Henninger's sulphone, but have got invariably this substance with a much lower melting-point.

The *Sodium Salt*, $C_6H_4ClCH_2SO_3Na$, was purified by evaporating the filtrate from the insoluble substance just described to dryness, boiling the residue with absolute alcohol to remove the organic salt from the sodic bromide, and finally recrystallizing from a very little water by spontaneous evaporation.

1.8405 gram of the salt dried *in vacuo* lost when heated to 160° 0.005 gram, corresponding to 0.27 per cent.

0.4160 gram lost at 160° 0.002 gram, corresponding to 0.48 per cent.

As one molecule of water corresponds to 7.30 per cent., it is evi-

* Potassic sulphite is to be preferred, however.

dent that the salt crystallizes without water, and the slight loss observed is due to a partial decomposition of the substance. This view is confirmed by the fact that the 1.8405 gram used in the first experiment lost only 1 mgr. when the temperature was not allowed to go above 100°.

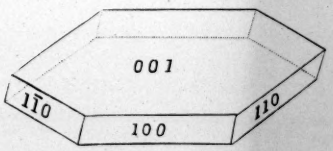
0.5650 gram of the salt dried at 160° gave by the method of Carius 0.3512 gram AgCl and 0.5804 gram $BaSO_4$.

	Calculated for $C_7H_6ClSO_3Na$.	Found.
Chlorine	15.54	15.37
Sulphur	14.00	14.11

Crystallized from water it forms large flat colorless crystals with pointed ends; from alcohol, pearly scales; it is freely soluble in water, but only sparingly in alcohol.

Dr. F. A. Gooch, who has had the kindness to examine the substance crystallographically for us, reports that "the crystals did not admit of measurement with the goniometer; but an examination of some of the smaller ones, under the microscope, between crossed Nicols, proved them to be triclinic (see figure); the planes of polarization of the Nicols making, in the case of a crystal lying upon its basal plane, angles of about 5° and 175°, or 85° and 95° respectively with the edge 100—001, when the plane of polarization of the ray from the polarizer remains unchanged. The apparent angles of the adjacent edges, when the crystal lies upon its basal plane, are approximately as follows:—

Edge 100—001	upon edge	110—001	. . .	141°
" 100—001	" "	$1\bar{1}0$—001	. . .	147°
" 110—001	" "	$\bar{1}10$—001	. . .	72°



The *Potassium Salt*, $C_6H_4ClCH_2SO_3K$, was made by adding potassic sulphate to the barium salt; the filtrate from the baric sulphate formed was evaporated to dryness, and the organic salt, dissolved out from the excess of potassic sulphate with absolute alcohol, purified by crystallization from water.

1.1328 gram of the salt dried *in vacuo* lost when heated to 160° 0.0075 gram, corresponding to 0.66 per cent.

As one molecule of water corresponds to 6.85 per cent. it is evident that this salt, like that of sodium, is free from water of crystallization.

0.3000 gram of the salt dried at 160° gave by the method of Carius 0.1760 gram AgCl.

0.3165 gram gave by the same method 0.3025 gram $BaSO_4$.

0.3065 gram gave, when heated with pure H_2SO_4, 0.1075 gram of K_2SO_4.

	Calculated for $C_7H_6ClSO_3K$	Found
Chlorine	14.50	14.50
Sulphur	13.08	13.13
Potassium	15.98	15.75

It resembles the sodium salt closely in appearance, but is much more soluble in alcohol. As, therefore, the separation of this salt from potassic bromide would be easier than that of the corresponding sodium compounds, it is better in making a salt of the sulphoacid from parachlorbenzylbromide to use potassic in place of sodic sulphite.

To prepare the other salts of the parachlorbenzylsulphoacid the mother-liquor of the sodium salt was treated with a small quantity of a solution of plumbic acetate, which precipitated plumbic bromide and sulphite; after these had been removed by filtration an excess of plumbic acetate threw down the lead salt of the sulphoacid, which was purified by recrystallization from water, and then decomposed with sulphuretted hydrogen; the filtrate from the plumbic sulphide was concentrated by evaporation, and the solution of parachlorbenzylsulphoacid thus obtained used in the preparation of the following salts.

The *Barium Salt*, $(C_6H_4ClCH_2SO_3)_2Ba.2H_2O$, was made by boiling the acid with pure baric carbonate. It can also be prepared by the addition of baric chloride to the sodium salt, but in this case it was found hard to free it from the excess of baric chloride.

0.9290 gram of the salt dried *in vacuo* lost when heated to 160° 0.0565 gram.

0.5408 gram lost 0.0332 gram.

	Calculated for $(C_7H_6ClSO_3)_2Ba.2H_2O$.	Found.	
Water	6.16	6.08	6.12

0.1575 gram of the salt dried at 160° gave, after precipitation with dilute H_2SO_4, 0.0680 gram of $BaSO_4$.

0.4620 gram gave 0.1995 gram $BaSO_4$.

	Calculated for $(C_7H_6ClSO_3)_2Ba$.	Found.	
Barium	25.00	25.38	25.39

It crystallizes from water in radiated bunches of white needles which are moderately soluble in water.

The *Calcium Salt*, $(C_6H_4ClCH_2SO_3)_2Ca.7H_2O$, was made by warming the aqueous solution of the acid with calcic carbonate, filtering and allowing the concentrated filtrate to evaporate spontaneously; it was purified by recrystallization from water.

0.5805 gram of the air-dried salt lost *in vacuo* 0.1033 gram; when heated to 160°, 0.0332 gram; making in all 0.1365 gram.

0.9536 gram lost *in vacuo* 0.1506 gram; when heated to 160°, 0.0552 gram; making in all 0.2058 gram.

	Calculated for $(C_7H_6ClSO_3)_2Ca.7H_2O$.	Found.	
Water	21.84	23.51	21.58

	Calculated for $(C_7H_6ClSO_3)_2Ca.2H_2O$.	Found.	
Water	7.39	6.96	6.87

The air-dried salt, therefore, contains seven molecules of water of crystallization, five of which it gives up *in vacuo*, while a heat of 160° is necessary to remove the whole of its water. The very high result of the first water determination was undoubtedly due to hygroscopic moisture in the air-dried salt.

0.6976 gram of the salt dried at 160° gave, after precipitation with ammonic oxalate and ignition over the blast-lamp, 0.085 gram of CaO.

	Calculated for $(C_7H_6ClSO_3)_2Ca$.	Found.
Calcium	8.87	8.70

It forms rhombic crystals so nearly square that they look like flattened cubes, freely soluble in water.

The *Copper Salt*, $(C_6H_4ClCH_2SO_3)_2Cu.2H_2O$, was made by warming the aqueous solution of the acid with pure cupric carbonate, and concentrating the filtrate on the water-bath; the crystals thus obtained were recrystallized from water.

0.7400 gram of the salt dried *in vacuo* lost when heated to 160° 0.0525 gram.

	Calculated for $(C_7H_6ClSO_3)_2Cu.2H_2O$.	Found.
Water	7.08	7.05

0.5000 gram of the salt dried at 160° gave by precipitation with sodic hydrate 0.0833 gram of CuO.

	Calculated for $(C_7H_6ClSO_3)_2Cu$.	Found.
Copper	13.37	13.30

It crystallizes in pale green needles grouped in bundles, and is readily soluble in water.

The neutral *Lead Salt*, $(C_6H_4ClCH_2SO_3)_2Pb.H_2O$, was made by treating an aqueous solution of the acid with plumbic hydrate not in excess, the solution was evaporated *in vacuo*, and the crystals washed with a little water to free them from the acid. It is probable from the resemblance in crystalline form, that the precipitate formed on adding a strong solution of the sodium salt to plumbic acetate consists of this salt.

0.8695 gram of the salt dried *in vacuo* lost when heated to 100° 0.0261 gram.

0.1910 gram lost at 100° 0.0056 gram.

0.1900 gram of the salt dried *in vacuo* gave, after precipitation with dilute H_2SO_4, 0.0902 gram of $PbSO_4$.

	Calculated for $(C_7H_6ClSO_3)_2Pb.H_2O$.	Found.	
Water	2.83	3.00	2.93
Lead	32.55	32.43	

0.1742 gram of the salt dried at 100° gave 0.0850 gram of $Pb.SO_4$.

	Calculated for $(C_7H_6ClSO_3)_2Pb$.	Found.
Lead	33.50	33.34

It crystallizes in long white needles grouped in sheaves or stars, which are not freely soluble in water.

Two *Basic Lead Salts* were obtained by treating the mother-liquor from the preceding salt with an excess of plumbic hydrate; one crystallized from water by spontaneous evaporation in little spheres made up of radiating needles, and seemed to be free from water of crystallization, although it blackened and lost weight at 160°.

0.3384 gram of the salt dried at 100° gave, after precipitation with dilute H_2SO_4, 0.2890 gram of $Pb.SO_4$.

	Calculated for $(C_7H_6ClSO_3)_4Pb_3O_2$.	Found.
Lead	58.35	58.34

The formula of this salt is therefore $(C_6H_4ClCH_2SO_3)_2Pb_2O$. The second salt, which crystallized from a hot concentrated solution in white scales, had the formula $C_6H_4ClCH_2SO_3PbOH.H_2O$.

0.2128 gram of the salt dried *in vacuo* lost at 120° 0.0087 gram.

0.2747 gram of the salt dried *in vacuo* gave with dilute H_2SO_4 0.1870 gram $PbSO_4$.

	Calculated for $C_7H_6ClSO_3PbOH.H_2O$.	Found.
Water	4.02	4.08
Lead	46.26	46.49

To obtain the *Free Acid* the lead salt, which had been purified with great care, was suspended in water, and decomposed with sulphuretted hydrogen, the filtrate from the plumbic sulphide formed was evaporated in a stream of sulphuretted hydrogen, first on the water bath, and finally at a still lower temperature, until it had attained the consistency of syrup; it was then put *in vacuo*, where, after standing some time, it crystallized in square plates, which, however, soon turned yellow, while fumes were given off which smelt of hydrochloric acid and benzaldehyd. These yellow crystals melted at 108°, but the evidences of decomposition were so marked that we do not consider this the true melting-point of the acid, nor did it seem worth while at present to follow the investigation of such an unstable substance farther.

The *Chloride*, $C_6H_4ClCH_2SO_2Cl$, was made by grinding the dry sodium salt, with phosphoric pentachloride, and afterward warming the mixture gently in a porcelain dish on the sand bath; the oily mass thus obtained gave with water the chloride as a heavy oil, which soon solidified, and was purified by crystallization from ether.

0.1410 gram of substance gave by the method of Carius 0.1768 gram of AgCl and 0.1470 gram of $BaSO_4$.

	Calculated for $C_7H_6ClSO_2Cl$.	Found.
Chlorine	31.55	31.02
Sulphur	14.22	14.32

It forms white flattened crystals, often arranged in indistinct pennate groups, and having an aromatic odor; melting-point 85½°; it is insoluble in water, soluble in ether and alcohol, but seems to be decomposed by the latter.

Parachlorbenzylsulphide, $(C_6H_4ClCH_2)_2S$.

Pauly* described this substance, which he obtained from chlorbenzylchloride (or bromide), by the action of an alcoholic solution of potassic sulphide, as a thick brown oil, with an unpleasant odor; and adds, that it did not solidify even after standing several days.

On warming an alcoholic solution of parachlorbenzylbromide with sodic sulphide (prepared by saturating one-half of an alcoholic solution of NaOH with H_2S, and then adding the other half) we obtained by precipitation of the product with water a heavy oil, which we dissolved in hot alcohol; on cooling this saturated solution a purer oil separated, that solidified on standing over night, and was then purified by recrystallization from hot alcohol.

0.2760 gram of the substance dried *in vacuo* gave on combustion 0.5970 gram of CO_2 and 0.1110 gram of H_2O.

	Calculated for $(C_7H_6Cl)_2S$.	Found.
Carbon	59.35	59.00
Hydrogen	4.24	4.47

It forms thick white needles, often seven centimetres long, with very little odor; from a hot alcoholic solution, it is sometimes deposited as an oil, which solidifies by scratching with a sharp glass rod; melting point, 42°; it cannot be sublimed without decomposition; essentially insoluble in water, soluble in cold, more freely in hot alcohol, easily soluble in ether, benzol, carbonic disulphide, and glacial acetic acid.

Diparachlorbenzylsulphone $(C_6H_4ClCH_2)_2SO_2$, was made by adding the calculated amount of chromic anhydride in small quantities at a time to the preceding substance, both bodies being dissolved in glacial acetic acid; the product of the oxidation, washed with water until free from compounds of chromium, was purified by crystallization from alcohol. The substance was also formed by the oxidizing action of the air on parachlorbenzylsulphide.

0.3510 gram of the substance gave, according to Carius, 0.3195 gram of AgCl and 0.2610 gram of $BaSO_4$.

	Calculated for $(C_7H_6Cl)_2SO_2$.	Found.
Chlorine	22.54	22.51
Sulphur	10.16	10.21

It crystallizes in very small needles, melts at 165°, and cannot be sublimed without decomposition; it is essentially insoluble in

* Pauly, Ann. Chem. Pharm. 167, 187.

water, readily soluble in alcohol, ether, carbonic disulphide, glacial acetic acid, and ligroine. The melting-point of this substance (165°) is essentially the same as that of the sulphone (167°), obtained in largest quantity by Vogt and Henninger from the action of chlorbenzylchloride on potassic sulphite, and mentioned on page 160. The isomere, melting at 149°, obtained by them, was probably the corresponding orthochlorbenzylsulphone, but it is hard to understand what the substance melting at 185° could have been. It will be remembered that we did not succeed in obtaining a sulphone when we repeated their work.

Parachlorbenzylmercaptan, $C_6H_4ClCH_2SH$.

The first attempt to prepare this substance was made in 1860 by Beilstein,* who heated a somewhat indefinite mixture of dichlor-substitution products of toluol with potassic sulphydrate, and obtained an oil which on exposure to the air yielded well-formed octahedra with a vitreous lustre, melting from the first preparation at 77°–78°, from the second at 84°–85°. Later, Neuhof† tried the same experiment with a mixture of ortho- and parachlorbenzyl-chloride, and confirmed the results of Beilstein, as the melting point of his crystals was 84°–85°. In repeating their work, we found that on mixing alcoholic solutions of parachlorbenzylbromide and KSH (prepared by saturating an alcoholic solution of potassic hydrate with sulphuretted hydrogen), heat was given off, and the action was finished without the aid of external heat in about half an hour; on adding water to the product, a dark-colored oil was precipitated, which, purified by distillation with steam, was frozen by immersion in ice and salt, and recrystallized from alcohol with the aid of a freezing mixture.

0.2560 gram of the substance dried *in vacuo*, treated by the method of Carius, gave 0.2276 gram of AgCl and 0.3750 gram of $BaSO_4$.

	Calculated for C_7H_8ClSH.	Found.
Chlorine	22.40	22.00
Sulphur	20.19	20.12

At ordinary temperatures, it is a colorless liquid with a most repulsive and nauseating smell; in a freezing mixture of ice and salt, it solidifies in white crystals, which melt from 19° to 20°. We are not certain that this is the true melting-point of the substance, as a

* Beilstein, Ann. Chem. Pharm. 116, 336. † Neuhof, Ann. Chem. Pharm 147, 339.

small portion of it may have been converted into the disulphide by the action of the air, and the elementary analysis cannot show the presence of this impurity, but the number here given cannot be very far from the truth, as we got in no case a melting-point much above 20°, and the substance was reduced with zinc and dilute sulphuric acid, so as to convert any disulphide into mercaptan, before taking some of the melting-points. It distils with steam, and mixes readily with alcohol, ether, benzol, and carbonic disulphide, but not with water. Yellow mercuric oxide attacks it with great energy, and converts it into the following compound:

Parachlorbenzylmercaptid $(C_6H_4ClCH_2S)_2Hg$, was purified by repeated crystallization from boiling alcohol.

0.4820 gram of the substance dried *in vacuo* gave by precipitation with H_2S 0.2175 gram of HgS.

	Calculated for $(C_7H_6ClS)_2Hg$	Found.
Mercury	38.84	38.91

It forms light white needles without odor, which seem to have no definite melting-point, although the substance turns red or black, and shrinks to about one-half of its original volume in the neighborhood of 160°; it is insoluble in water, very slightly soluble in ether, benzol, carbonic disulphide, glacial acetic acid, and cold alcohol; more readily, but still not very freely, soluble in hot alcohol. It is decomposed by sulphuretted hydrogen into mercuric sulphide and the mercaptan.

Parachlorbenzyldisulphide, $(C_6H_4ClCH_2)_2S_2$.

This substance was made in several different ways:—(1) When parachlorbenzylbromide was boiled for two or more days with an alcoholic solution of potassic sulphydrate, on evaporating off the alcohol a mixture of the oily mercaptan with needles of the disulphide was obtained, which was exposed to the air for some time to oxidize the mercaptan. (2) The parachlorbenzylmercaptan was treated with the calculated amount of bromine dissolved in ether; the reaction is as follows:

$$2C_7H_6ClSH + Br_2 = (C_7H_6Cl)_2S_2 + 2HBr.$$

When a large excess of bromine was added, the product was an oil with an aromatic smell, the study of which is postponed for the present. (3) Parachlorbenzylbromide was warmed with an alco-

holic solution of sodic disulphide (Na_2S_2) obtained by dissolving the calculated amount of flowers of sulphur in an alcoholic solution of sodic sulphide (Na_2S). The products of all these methods had the same melting-point and properties.

For analysis, a specimen prepared according to the first method was purified by crystallization from alcohol and dried *in vacuo*.

0.3925 gram of the substance gave on combustion 0.7615 gram of CO_2 and 0.1475 gram of H_2O.

0.2540 gram gave, according to the method of Carius, 0.3780 gram of $BaSO_4$.

	Calculated for $(C_7H_6Cl)_2S_2$.	Found.
Carbon	53.34	52.91
Hydrogen	3.81	4.17
Sulphur	20.32	20.44

It forms flattened white needles with a disagreeable smell, somewhat like that of the mercaptan, but much less nauseating: melting-point 59°; insoluble in water, readily soluble in alcohol, glacial acetic acid, and ligroine, very soluble in ether, benzol, and carbonic disulphide. Neither mercuric oxide nor mercuric chloride has any action upon it. Nascent hydrogen made from zinc and dilute sulphuric acid converts it into the mercaptan.

Beilstein, and afterward Neuhof, obtained their so-called mercaptan (melting-point 84°–85°) by boiling the substances together for a long time, which we find, as already stated, gives the disulphide as principal product; furthermore, their crystals were formed only after long exposure of the liquid product of the reaction to the air. It would seem, therefore, that their substance must have been the disulphide, the percentage composition of which is essentially the same as that of the mercaptan, and therefore the two substances could not be distinguished by analysis, but only by treatment with mercuric oxide, which they do not seem to have tried. On the other hand, the melting-point of their substance (84°) is much higher than that of ours (59°), and it is certainly strange that a mixture of an ortho- and para-compound should melt at a higher temperature than the pure para-compound; they also describe it as crystallizing in vitreous octahedra, while our substance crystallizes even by slow evaporation of a benzole solution in the flattened needles already mentioned.

Parachlorbenzyldisulphidedioxide, $(C_6H_4ClCH_2)_2S_2O_2$, was made by adding the necessary amount of chromic anhydride dissolved in

glacial acetic acid to a weighed quantity of the disulphide also dissolved in glacial acetic acid; on the addition of water, an oil was deposited, which became solid on standing in the cold, and was purified by crystallization from alcohol.

0.5870 gram of the substance dried *in vacuo* gave, by combustion, 1.0390 gram CO_2 and 0.1838 gram of H_2O.

	Calculated for $(C_7H_6Cl)_2S_2O_2$.	Found.
Carbon	48.42	48.27
Hydrogen	3.45	3.48

It is a waxy solid, which becomes crystalline after some time; the melting-point of the specimen analyzed was 120°; it is insoluble in water, readily soluble in alcohol, ether, benzol, carbonic disulphide, and glacial acetic acid.

The *Parachlorbenzylethylether* was made by boiling parachlorbenzylbromide with an alcoholic solution of sodic hydrate; the product was precipitated with water, and the oil purified by distillation with steam. It was a colorless liquid, which distilled over between 215°–225°, and did not solidify when cooled to —12°. As its properties therefore agreed essentially with those ascribed to it by Naquet,* who made it as we did, and Neuhof,† who obtained it from the chlorbenzylacetate and alcoholic potassic hydrate, we did not think it worth while to analyze or study it more carefully.

We have thus brought our revision of the parachlorbenzyl compounds to an end; the only one previously obtained that we have not studied is the amide of the parachloralphatoluylic acid, which we did not succeed in obtaining by the action of potassic cyanide on parachlorbenzylbromide, although Neuhof made it in this way from the chlorbenzylchloride. It is possible, but not very probable, that this difference between his results and ours is due to the fact that he used the chloride while we used the bromide.

For convenience of comparison, the melting-points of the substances described in this paper, with those given by our predecessors, are collected in the following table, to which is added a comparison between the amounts of water of crystallization in the salts of the parachlorbenzylsulphoacid, in those heretofore described as such, and in the corresponding salts of the benzylsulphoacid.‡

* Naquet, Ann. Chem. Pharm., Supp. 2, 249. † Neuhof, Ann. Chem. Pharm. 147, 339.
‡ Bohler, Zeitschrift der Chemie, 1868, 449.

Comparison of Melting-points.

Formula of Substance.	Correct Melting-point.	Former Melting-point.	Authority for former Melting-point.
$C_6H_4ClCH_2SO_2Cl$	85½°		
$(C_6H_4ClCH_2)_2S$	42°	Oil	Pauly.
$(C_6H_4ClCH_2)_2SO_2$	165°	167°	Vogt and Henninger.
$C_6H_4ClCH_2SH$	19°	77°–78°	Beilstein.
		84°–85°	....
		84°–85°	Neuhof.
$(C_6H_4ClCH_2)_2S_2$	59	See above.	
$(C_6H_4ClCH_2)_2S_2O_2$	120°		
$C_6H_4ClCH_2OC_2H_5$	Oil	Oil	Naquet.
		Oil	Neuhof.

Comparison of the Composition of certain Salts of Chlorbenzyl and Benzyl Sulphoacids.

Name of Salt.	Chlorbenzylsulphoacid.			Benzyl Sulphoacid.
	Para.	Bohler.	Vogt and Henninger.	
Sodium	No H_2O	....	....	....
Potassium	No H_2O	H_2O	H_2O	H_2O
Barium	$2H_2O$	H_2O	H_2O	$2H_2O$
Calcium	$7H_2O$ or $2H_2O$	....	....	$2H_2O$
Copper	$2H_2O$	....	....	No good crystals.
Lead	H_2O	....	....	No H_2O
Basic Lead	$PbO_2H_2.2H_2O$	PbO_2H_2	....	PbO_2H_2
Basic Lead	2PbO	....	....	....

PRELIMINARY NOTE ON THE SYNTHESIS OF METHYLCONINE AND CONSTITUTION OF CONINE.

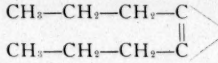
By Arthur Michael and Charles Gundelach.

The action of alcoholic ammonia on normal butylaldehyde was examined in 1871–2 by H. Schiff, who obtained, on allowing a mixture of these compounds to stand for six months and heating subsequently the bases thus formed to a high temperature, among

other products a tertiary base, isomeric with conine, and which he called paraconine. We have obtained this base more easily by heating normal butylidene chloride (CH_3-CH_2-CH_2-$CHCl_2$) with alcoholic ammonia for six hours at 180°, and have characterized the base obtained as paraconine, by an analysis of the platinum salt, its behavior toward chlorhydric acid, and by the formation of a liquid addition-product with ethyl iodide.

Of greater interest is the result obtained in the action of an alcoholic solution of methylamine on normal butylidene chloride, under the same conditions as above. The base thus formed appears to be identical with natural methylconine. This we infer from its physical properties and analysis, behavior toward chlorhydric acid, and especially from the formation of a solid addition-product by heating it on a water-bath with ethyl iodide and alcohol, which is apparently identical with the ammonium iodide compound obtained by von Planta and Kekulè in the same manner from natural methylconine.

These and other experiments, which we have made in the hope of ascertaining the constitution of conine, have led us to accept the following rational formula as the most probable for conine:



Methylconine being a tertiary base, the amine hydrogen is replaced in the formula by a methyl group. Should a more thorough investigation of the base show that it is identical with methylconine, this would be the first instance of a synthesis of a natural alkaloid, since the product found in nature consists of a mixture of conine and methylconine. Possibly, by distilling the chloride of methylconine in a current of chlorhydric acid, the synthesis of conine may be effected.

This research will, owing to the difficulty of obtaining the crude products and the small yield obtained of the base, proceed slowly; and we hope by this note to reserve the study of the reaction in question.

LABORATORY NOTES FROM THE UNIVERSITY OF CINCINNATI.

XIII.—ON A NEW VARIETY OF TETRAHEDRITE.

By F. W. Clarke and Mary E. Owens.

Some months ago there was submitted to one of us for investigation a mineral from an unknown locality in Arizona. It was massive, steel-gray in color, and bore all the ordinary characteristics of tetrahedrite. Its specific gravity, however, was a trifle lower than is usual for the species, ranging from 4.34 to 4.36. Mixed with it were trifling quantities of galena, copper pyrites and a quartzose gangue. An analysis of the mineral, carefully freed from impurities, led to the following results:

	I.	II.	III.	IV.	Mean.
S	21.67	.....	.....	.....	21.67
Sb	.....	24.57	24.86	.....	24.72
Cu	.....	33.68	.....	33.38	33.53
Pb	.....	15.73	16.72	.....	16.23
Ag	1.78	.....	.....	1.82	1.80
Fe	.....	.....	.....	.56	.56
					98.51

A trace of arsenic was not estimated; nor was any account taken of a fraction of one per cent. of gangue from which the mineral could not be perfectly separated. Another analysis was begun by Mr. H. B. Wilson, but not finished. His figures were unfortunately lost, and we can only say concerning them that his estimate for sulphur closely confirmed the value given above.

It will at once be seen that this mineral agrees in composition with no species hitherto described. Its density, however, and its atomic ratios, clearly identify it as tetrahedrite in which a portion of the copper has been replaced by lead. The high percentage of the latter metal might be attributed to an admixture of galena were it not for the low specific gravity. It might perhaps be regarded as an independent species, in which case its claims to recognition would be precisely analogous to those of the other derived tetrahedrites, freibergite and spaniolite.

XIV.—SPECIFIC GRAVITY DETERMINATIONS.

By F. W. Clarke.

The following determinations of specific gravity have been made by students under my immediate supervision. The salts were weighed in benzol, and the density of water at 4° has been taken as unity. To each figure, which is the mean of several closely concordant estimations, I append the name of the determiner.

Ammonium perchlorate,	NH_4ClO_4	1.885	at 25°	A. Stephan.
Barium dithionate,	$BaS_2O_6.4H_2O$	3.055	24.5°	"
Magnesium iodate,	$MgI_2O_6.4H_2O$	3.283	13.5°	E. P. Bishop.
Barium bromide,	$BaBr_2.2H_2O$	3.680	24.3°	A. Harper.
Barium cadmium bromide,	$BaCdBr_4.4H_2O$	3.665	24°	"
Barium iodide,	$BaI_2.7H_2O$	3.673	20.3°	H. W. Leonard.
Cadmium potassium iodide,	$K_2CdI_4.2H_2O$	3.359	21°	"
Cobalt hypophosphite,	$CoP_2H_4O_4.6H_2O$	1.809	18.5°	G. C. Nye.
Nickel "	$NiP_2H_4O_4.6H_2O$	1.841	19.3°	"
Zinc "	$ZnP_2H_4O_4.6H_2O$	2.017	19.6°	"
Ammonium sulphate,	$(NH_4)_2.SO_4$	1.765	20.5°	H. B. Wilson.
Trimercuric chromate,	$3HgO.CrO_3$	7.1711	18.6°	Helena Stallo.
Manganese oxalate,	MnC_2O_4	2.444	21.4°	L. R. Freeman.
Cobalt "	CoC_2O_4	2.310	19.8°	"
Nickel "	NiC_2O_4	2.227	19°	"
Cadmium "	CdC_2O_4	3.315	17.5°	"
Zinc "	ZnC_2O_4	2.564	20.1°	H. B. Wilson.
Stannous "	SnC_2O_4	3.573	21.3°	"
Oxalic acid,	$H_2C_2O_4.2H_2O$	1.653	18.5°	"
Roseocobalt iodosulphate,	$Co_2(NH_3)_{10}(SO_4)_2I_2$	2.144	20.5°	"
Cadmium formate,	$CdC_2H_2O_2.2H_2O$	2.429	20°	H. Breen.
Zinc "	$ZnC_2H_2O_2.2H_2O$	2.157	21.3°	"
Cadmium barium formate,	$(BaCd)C_2H_2O_2$	2.733	19.7°	"
Barium formate,	$BaC_2H_2O_2$	3.471	23°	D. Stern.
" propionate,	$BaC_6H_{10}O_2$	2.067	22.3°	"
" butyrate,	$BaC_8H_{14}O_2$	1.768	22°	"
Diammonic citrate,	$(NH_4)_2C_6H_6O_7$	1.479	22°	R. S. Blakemore.
Trisodic "	$2(C_6H_5Na_3O_7).11H_2O$	1.858	23.8°	"
Barium tartar emetic,	$BaC_4H_4SbO_{14}.2H_2O$	3.112	19°	O. T. Joslin.
Barium tartrate,	$BaC_4H_4O_6$	2.973	21.4°	"
Lead "	$PbC_4H_4O_6$	4.012	17.2°	"
Strontium "	$SrC_4H_4O_6$	2.582	17.3°	"
" "	$SrC_4H_4O_6.4H_2O$	1.966	19.8°	"
Cobalt thiosulphate,	$CoS_2O_3.6H_2O$	1.935	25°	D. S. Oliver.
Magnesium "	$MgS_2O_3.6H_2O$	1.818	24°	"
Ammonium copper chloride,	$2NH_4Cl.CuCl_2.2H_2O$	1.984	24°	C. S. Evans.
" " sulphate,	$2(NH_4)_2SO_4.CuSO_4.6H_2O$	1.871	22°	"
Copper ammonio-sulphate,	$CuSO_4.4NH_3.H_2O$	2.133	24.3°	"
" ammonio-nitrate,	$CuN_2O_6.4NH_3$	1.905	21.5°	"

The subjoined determinations were made by myself:

Thorium sulphate,	$Th(SO_4)_2$	4.053 at	22.8°
" "	$2Th(SO_4)_2.9H_2O$	3.398	24°
" oxalate,	ThC_4O_8	4.637	16°
Strychnine,		1.359	18°
Strychnine chloroplatinate,		1.779	13.5°
Berberine hydrochlorate,		1.397	19.4°
" chloroplatinate,		1.758	19°
Ethylamine "		2.252	19.1°

CONCERNING IODINE.

By Victor Meyer.*

While reserving the right to consider in detail the criticism of my experiments on iodine which Messrs. Crafts and Meier have given in their extremely interesting paper on "The Vapor Density of Iodine," I take this opportunity to communicate briefly the following observation: By a modification of the method of heating I have succeeded in reaching a materially higher temperature than that which has thus far been employed by me in estimating vapor densities. At the temperature now attainable for heating the vessels, iodine has no longer the density corresponding to I_2, but it agrees very closely with the value calculated for I. That the method of heating and of the experiment in general are capable of giving accurate results was first established by making an estimation of the vapor density of mercury under exactly the same conditions as those which existed in the experiments described below. This gave:

$S = 0.0861$; $t = 15.3°$; $B = 716.9$ mm.; $V = 10.8$.

Found.	Calculated for Hg.
7.03	6.91

The estimations made with iodine gave the following results:

I. $S = 0.0642$; $t = 16°$; $B = 718.2$ mm.; $V = 12.5$.
II. $S = 0.0639$; $t = 15°$; $B = 717.0$ mm.; $V = 12.35$.
III. $S = 0.0600$; $t = 21°$; $B = 722.5$ mm.; $V = 11.8$.

*Communicated to this Journal.

Found.		
I.	II.	III.
4·53	4·55	4·57

The calculated values are for $\begin{cases} I_2 = 8.79 \\ \frac{2}{3}I_2 = 5.83 \\ I = 4.39. \end{cases}$

The question whether, in accordance with the view of Mr. Crafts, the minimum density is reached in the value for I (4.39), or whether, as is assumed in the chlorogen-hypothesis * suggested by me, the limit of dissociation is given in the value $\frac{2}{3}I_2$ (2.93), may be tested by vapor density determinations made at still higher temperatures than that already reached. I hope to reach the temperatures necessary for these experiments by the use of the oil blast-furnace recently described by Deville and Troost, in which porcelain may be melted; and I hope to be able to use graphite for the vessels in case it should be found impossible to use porcelain.

I can not close this communication without expressly stating that the credit of having first distinctly exceeded the dissociation maximum of $\frac{2}{3}I_2$, previously reached by me, undoubtedly belongs to Mr. Crafts.

ZURICH, *May*, 1880.

ON THE DETERMINATION OF BARIUM AS CHROMATE.

BY H. N. MORSE.

As a means of estimating barium in the presence of strontium, calcium and magnesium, F. Frerichs† recommends precipitation from solutions containing acetic acid by means of chromate of potassium, collection of the precipitate upon a weighed filter, and washing with dilute acetic acid until a colorless filtrate is obtained. The method having yielded, in the hands of our students, very unsatisfactory results, it was decided to subject it to a careful examination. The work is still incomplete; but in view of the fact that it has been necessarily suspended for a few months, it is thought best to briefly record the results thus far obtained.

*Chem. Centralblatt, 1879, 577. †Ber. d. d. ch. Gesell. 1874, 800, 956.

Solutions of the pure chlorides of barium, strontium and calcium were prepared, and the strength of each carefully determined. The acetic acid used was proved to be free from hydrochloric and sulphuric acids, and its strength was ascertained by means of a standard solution of caustic potassa. The chromate of potassium employed was purchased as chemically pure, and assumed to be so after three recrystallizations. The filters were of the best Swedish paper, and had been soaked in very dilute hydrochloric acid. They were in all cases dried three hours at a temperature between 110° and 115°, and as nearly as possible at 112°. When the variation in weight after two successive heatings amounted to less than half a milligram the mean was assumed to be correct. If the variation amounted to more than half a milligram the heating was repeated until three weights whose greatest divergence was less than a milligram were obtained. The mean of the three was then taken. The weighing glasses used were found to vary in weight from day to day according to the humidity of the atmosphere. The maximum variation observed was about one milligram. The weighings obtained are therefore believed not to be reliable to within less than one milligram, since no analysis could be completed in a single day. It was discovered too late to repeat the work that the results are vitiated to some extent by the presence of a minute quantity of sulphate in the chromate of potassium, and by the fact that the filters used lose weight when washed with acetic acid of any considerable strength. The vitiation from these causes is not, however, sufficient to destroy their value as preliminary results.

Frerichs states that the presence of acetic acid is a necessary condition to the complete precipitation of the barium as chromate, and the two following experiments tend to prove the correctness of this observation. 10 c. c. of the standard solution of barium chloride were in each case diluted with water, treated with double the quantity of potassium chromate required by the barium and allowed to stand about forty-eight hours. The precipitates were then collected upon weighed filters and thoroughly washed with water. The weights found were 0.2313 gram and 0.2322 gram, while the calculated weight was only 0.2291 gram. The excess in the first case is 0.0022 and in the second 0.0031 gram. Nevertheless both filtrates became quite cloudy on being treated with dilute sulphuric acid, showing that the barium had not been completely precipitated.

The next step was to ascertain whether the precipitation of the barium is complete in the presence of acetic acid. To this end several portions of ten or twenty c. c. of the standard solution of barium chloride were measured off, diluted with water, and treated with about five c. c. of thirty per cent. acetic acid and double the quantity of chromate of potassium required by the barium. After about forty-eight hours the precipitates were collected upon weighed filters and thoroughly washed with water. The following results were obtained :

$BaCl_2$ taken.	$BaCrO_4$ calc.	$BaCrO_4$ found.	Difference.
I. 10 c. c.	0.2291 gr.	0.2289 gr.	0.0002 gr.
II. "	"	0.2278	0.0013
III. 20 c. c.	0.4582 gr.	0.4570	0.0012
IV. "	"	0.4575	0.0007

The solubility of the chromate of barium in acetic acid was then examined into. In all of these experiments the precipitate was washed with the prepared liquid until the volume of the filtrate reached 250 c. c. The filtrate was then allowed to pass again through the filter. The portions of chromate of barium first experimented upon were those marked I. and II. in the above table. The wash liquid used was a one per cent. acetic acid.

Precipitate I. lost by the first washing 0.0248 gram, or 10.87 per cent.; by the second 0.0229 gram, or 11.22 per cent.

Precipitate II. lost by the first washing 0.0244 gram, or 10.71 per cent.; by the second 0.0282 gram, or 13.81 per cent.

The filtrates were clear, but decidedly yellow in color, and gave precipitates of sulphate of barium on being treated with dilute sulphuric acid.

It appears from these results that, though barium can be completely precipitated in the presence of acetic acid by chromate of potassium, the precipitate cannot be washed with even the dilutest solutions of acetic acid without loss. The only possible explanation of this apparent contradiction is that the chromate of barium is in the first case prevented from going into solution by the presence of an excess of chromate of potassium; and, if so, it should not dissolve when washed with acetic acid containing chromate of potassium. In order to test the correctness of this explanation, known weights of chromate of barium were washed with solutions of acetic acid of various concentrations, and containing different quantities

of chromate of potassium. As before, the precipitates were washed until the volume of the filtrate reached 250 c. c., after which the filtrate was allowed to pass again through the filter. The following results were obtained:

Experiment A.

Weight of chromate of barium, 0.2278 gram.

Wash liquid, 1 per cent. acetic acid containing about six molecules of chromate of potassium to each one hundred molecules of the acid.

Loss in weight, 0.0001 gram.

Experiment B.

Weight of chromate of barium, 0.45695 gram.

Wash liquid, 2 per cent. acetic acid containing about three molecules of chromate of potassium to each one hundred molecules of the acid.

Loss in weight, 0.0008 gram.

Experiment C.

Weight of chromate of barium, 0.4561 gram.

Wash liquid, 10 per cent. acetic acid containing about one molecule of chromate of potassium to each one hundred molecules of the acid.

Loss in weight, 0.0035 gram.

Experiment D.

Weight of chromate of potassium, 0.4575 gram.

Wash liquid, 10 per cent. acetic acid containing about ½ molecule of chromate of potassium to each one hundred molecules of the acid.

Loss in weight, 0.0031 gram.

Experiment E.

Weight of chromate of barium, 0.4544 gram.

Wash liquid, 10 per cent. acetic acid containing about two molecules of chromate of potassium to each one hundred of the acid.

Loss in weight, 0.0039 gram.

Experiment F.

Weight of chromate of barium, 0.4505 gram.

Wash liquid, 20 per cent. acetic acid containing about one mole-

cule of chromate of potassium to each one hundred molecules of the acid.

Loss in weight, 0.0039 gram.

In the experiments C, D, E and F, the loss in weight would seem to indicate that the chromate of barium had been to some extent dissolved by the acetic acid, notwithstanding the presence of the chromate of potassium. But this is believed not to have been the case. The filtrates remained perfectly clear when treated with dilute sulphuric acid, though allowed to stand in some instances more than three weeks. Moreover it was found that a single milligram of barium is sufficient to produce an immediate and persistent cloudiness in 250 c. c. of 20 per cent. acetic acid containing one molecule of chromate of potassium to each one hundred of the acid and a little sulphuric acid. The filtrates must therefore have contained in every instance less than one milligram of barium.

On examining into the other possible causes of loss in weight, it was discovered that the chromate of potassium employed contained a small quantity of sulphate, and that the filters lost weight to a slight extent when washed with ten and twenty per cent. solutions of acetic acid containing chromate of potassium. The loss from the first cause is believed to have been insignificant, since the quantity of sulphate contained in the chromate was very small, and the decomposition of the chromate of barium by a sulphate is very slow. This decomposition may, however, have been somewhat accelerated by the presence of acetic acid. The loss from the second cause may have been more considerable, since some of the papers experimented upon diminished two and a half milligrams in weight.

The experiments here recorded are to be regarded as preliminary only. The work will be resumed at the earliest opportunity. The results thus far obtained indicate: (1) That barium can be precipitated in the presence of acetic acid by an excess of chromate of potassium nearly, if not quite, as completely as by sulphuric acid; (2) That the precipitate cannot be washed with pure solutions of acetic acid, however dilute; (3) That, if a small quantity of chromate of potassium is added, the precipitate can be washed with quite concentrated solutions of acetic acid without undergoing solution. By using a wash liquid of acetic acid containing chromate of potassium it is probable that barium can be readily and completely separated from strontium, calcium and magnesium. It

is reasonable to suppose that any other soluble chromate would protect the barium compound equally well; indeed it is only on the basis of such a supposition that the results reported by Frerichs can be even partially explained. He must have ceased washing with dilute acetic acid as soon as the last traces of chromate of strontium, calcium or magnesium had passed into the filtrate; for otherwise there would have been a deficiency of barium. The observation that a colorless filtrate can be obtained by washing chromate of barium with dilute acetic acid must have been erroneous.

JOHNS HOPKINS UNIVERSITY, *June*, 1880.

ON *A*-TOLUENEDISULPHONIC ACID AND ITS DERIVATIVES.

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In a previous communication* it was stated that when toluene-parasulphochloride is treated with fuming or concentrated sulphuric acid, *a*-toluenedisulphonic acid is formed. It was shown that this acid is identical with the acid obtained by Blomstrand,† who had prepared it in a different way. It remained to ascertain the positions of the two sulpho-groups in the acid, as its structure had not been determined. For this purpose the following investigation was undertaken.

It would be a simple matter to decide this question if toluene-orthosulphochloride should upon treatment with sulphuric acid give the same product as the para-compound in the previously described experiment. It was thought at first that Blomstrand's second product might have been derived from the ortho-compound, and was not a consequence of the high temperature at which he worked, and to which he ascribed the formation of the *p*-toluene-disulphonic acid. If my explanation could be shown to be true, then the attempt to solve the question proposed above would have proved fruitless. Another obstacle presented itself in the statement made by Beckurts,‡ that the mixed toluenemonosulphonic acids

* This Journal, 1, 170. † Ber. d. deutsch. Ges. 5, 1084. ‡ Ber. d. chem. Ges. 10, 943.

which had been used in Blomstrand's experiment consisted not only of two, but of three isomeric monosulphonic acids. This evidently would have complicated the investigation in question, had it not been found that Beckurts' statements in regard to the third isomer were wrong,* and that his meta-acid consisted of a mixture of the ortho- and para-acids. In regard to Blomstrand's experiment there was very little doubt that his second disulphonic acid had resulted, as supposed by himself, in consequence of the high temperature. To prove this beyond any doubt, the following experiments were performed at temperatures not exceeding 150°.

I. Almost pure, solid toluneparasulphochloride and fuming sulphuric acid were allowed to act upon each other at a temperature of 140–150° for about three hours. After the reaction had ceased, and the hydrochloric acid had been gradually given off, the mass was diluted with water and subsequently treated with barium carbonate. The filtrate from barium sulphate gave, on evaporation, an easily soluble barium salt, which was converted into the potassium salt. The first two crops of crystals were almost pure potassium *α*-toluenedisulphonate. Then it became advisable to evaporate the last mother-liquor to dryness, and to wash the residue with alcohol in order to remove the unchanged potassium toluenemonosulphonate. The potassium monosulphonate is very easily soluble in alcohol, whereas potassium *α*-disulphonate is almost insoluble in alcohol of 93–95 per cent. On dissolving the residue on the filter in water, more potassium *α*-toluenedisulphonate was obtained, and not a trace of another compound, showing that Blomstrand's *β*-disulphonic acid had not been formed under these circumstances. An analysis of the pure toluenedisulphonate of potassium gave the following results:

I. 0.35 gram gave 0.471 gram $BaSO_4$ = 0.0647 gram S.

II. 0.33675 gram lost 0.018 gram H_2O at 200°.

III. 0.3371 gram gave 0.16725 gram K_2SO_4 = 0.0751 gram K.

		Calculated.		Found.
$C_7H_6O_6$	...	186.	53.44	
S_2	...	64.	18.49	18.50
K_2	...	78.26	22.60	22.30
H_2O	...	18.	5.47	5.31
		346.26	100.00	

* This Journal, 1, 170.

From the pure potassium salt and phosphorus pentachloride the chloride of the acid was obtained in nearly theoretical quantity. It was washed with water and recrystallized from ether. It fused at 52°.

The pure chloride treated with aqueous ammonia gave the disulphamide, fusing at 186–187°. It was noticed that the chloride is attacked with difficulty by aqueous ammonia, in consequence of which the reaction required to be facilitated by the use of a water-bath. It has been found, however, that in the formation of the amide from the chloride and aqueous ammonia the reaction is not a clean one, only 30–40 per cent. being obtained; whereas, when a strong alcoholic solution of ammonia is employed no heat is required, and a much larger yield is obtained. The amide is very soluble in an excess of ammonia, and the solution has to be freed from the excess before the amide will separate out.

The secondary reaction which was noticed in the formation of the disulphamide seems to be due to the replacement of one chlorine atom by ONH_4, and of the other by NH_2, though the analysis of the barium salt disclosed no relation with an acid of the formula $C_6H_3\begin{cases}CH_3\\SO_2OH\\SO_2NH_2\end{cases}$. The barium salt which was analyzed can be obtained if the mother-liquor from the preparation of the disulphamide is boiled with litharge for several hours, until it ceases to give off ammonia, when ONH_4 is changed into Opb, and the NH_2 remains unaltered. On adding to the filtrate, first, sulphuric acid and then barium carbonate, a barium salt of a syrupy appearance can be obtained. This has to be separated from $C_6H_3\begin{cases}CH_3\\(SO_2O)_2Ba\end{cases}$ with alcohol, which leaves the latter undissolved. The evaporated alcoholic filtrate was dried at 150°, and of the amorphous, though not hygroscopic residue, a barium determination was made which gave 10.7 per cent. Ba. From the analysis it appears that the product is not $C_6H_3\begin{cases}CH_3\\SO_2Ba\\SO_2NH_2\end{cases}$, but a compound of different composition, containing barium and nitrogen. It is possible that an acid of the formula $C_6H_3\begin{cases}CH_3\\SO_2OH\\SO_2NH_2\end{cases}$ can be prepared from the disulphamide by boiling with hydrochloric acid, as the two sulphamide groups may show a marked difference in their conduct towards

hydrochloric acid. One of the groups in the benzoic acid series can be easily changed with hydrochloric acid into a sulpho-group, whereas the same transformation does not take place in the other. The different behavior of the two groups will be discussed more fully when I come to speak of the disulpho-derivatives of benzoic acid.

II. Liquid toluneorthosulphochloride was now subjected to the same treatment with fuming sulphuric acid at a temperature of 135°. On examining the product, however, it gave the same salts, chloride and amide, as described under I. From 100 grams of the chloride not a trace of a second acid could be obtained. It was noticed that the reaction with sulphuric acid occurred in less time, and at a slightly lower temperature. The yield was better, and the potassium salt required less washing with alcohol than in the previous experiment with the para-compound, but it was darker colored, owing to the fact that the liquid chloride is always darker than the solid sulphochloride.

It is evident from these experiments then, that the second acid of Blomstrand was not formed from orthosulphochloride at 135°, but must have been formed in consequence of the temperature, which was carried to 180° in his experiment. It is, moreover, not improbable that at this high temperature a trisulphonic acid was formed, as he made no analysis to confirm his view that a second disulphonic had actually been formed. Blomstrand also expressed the view that the toluenedisulphonic acid, prepared by C. Senhofer,* is different from his acid, but that statement requires, as I think, confirmation. It has been shown in the course of these experiments that the two monosulphochlorides, one of which belongs to the ortho and the other to the para series, yield one and the same disulphonic acid. This furnishes the proof of the structure of *a*-toluenedisulphonic acid, according to which the positions of the two sulpho-groups are 2 and 4 with reference to the CH_3 group. Hence the formula for *a*-toluenedisulphonic acid is $C_6H_3\begin{cases} CH_3 & (1). \\ SO_3OH & (2). \\ SO_3OH & (4). \end{cases}$ Other confirmatory experiments to complete the proof of the structure of this acid will be given below.

* Liebig's Annal. 164, 126.

Oxidation of 1, 2, 4 Toluenedisulphamide.

The amide which fuses at 186–187° was subjected to oxidation with permanganate of potassium. The following proportions were used: 1 part of the amide, 5 parts of potassium permanganate were dissolved in 100 c. c. of water. The mixture was heated on a water bath for several hours. It was found that 4 to 5 hours were sufficient to complete the oxidation. The solution was then decolorized with alcohol, filtered and evaporated to a small volume. After the addition of hydrochloric acid a colorless compound separated. It was recrystallized from water. From a saturated solution it is obtained as a fine crystalline powder, and in small rhombic plates from a dilute solution. The yield thus obtained weighed half as much as the toluenedisulphamide employed.

The fine powder and the rhombic plates were analyzed separately with the same results.

Fine crystalline powder:

I. 0.32875 gram of the substance gave 0.5905 gram $BaSO_4$ = 0.0819 gram S.

II. 0.3168 gram of the substance gave 0.5682 gram $BaSO_4$ = 0.07804 gram S.

III. 0.3119 gram substance gave 29 c. c. N at 17° at 765 mm. barom. = 0.033786 gram N.

Small rhombic plates:

IV. 0.3292 gram substance gave 0.59075 gram $BaSO_4$ = 0.0811 gram S.

	Calculated.		Found.			
			I.	II.	III.	IV.
$C_7H_7O_5$ ...	170	54.89				
S_2 ...	64	24.43	24.66	24.63	...	24.63
N_2 ...	28	10.68			10.83	
	262	100.00				

It was expected that the substance would be a compound of the same class of bodies to which Prof. Remsen and myself had ascribed the name "sulphinide."* This expectation was fully justified. The analysis corresponds to the formula $C_6H_3\begin{cases}CO\\SO_2NH\end{cases}$, and $C_6H_3\begin{cases}CO\\SO_2NH_2\end{cases}$,

* This Journal, 1, 426.

its name is hence sulphaminebenzoic sulphinide. The same condensation has taken place here which has been noticed in a number of cases since, whenever a sulphamide group is located in an ortho position with reference to a carboxyl group. This is the more significant, as there has been no case recorded in which this law does not hold good.

Sulphaminebenzoic sulphinide, $C_6H_3\begin{cases}CO\neg\\SO_2NH\\SO_2NH_2\end{cases}$ (or paraanhydrodisulphaminebenzoic acid), crystallizes, as above described, from water. It is more easily soluble in hot water. It is difficultly soluble in cold water, and almost insoluble in cold hydrochloric acid; but if the aqueous solution is boiled for any length of time in the presence of hydrochloric acid, sulphaminebenzoic sulphinide is transformed into sulphaminesulphobenzoic acid, which will be described fully below. It is very difficult to avoid a partial change when the product obtained by the addition of hydrochloric acid is recrystallized, unless the hydrochloric acid is entirely removed by drying in the air at ordinary temperature. Alcohol and ether dissolve it very easily without change, even in the presence of hydrochloric acid. It fuses at 285° (uncorr.), but undergoes at the same time partial decomposition.

Phosphorus pentachloride does not act upon sulphaminebenzoic sulphinide, either at the ordinary temperature or when heated. This fact proves the absence of a hydroxyl group in the compound.

The aqueous solution of sulphaminebenzoic sulphinide has acid properties. When it is neutralized with different carbonates, corresponding salts can be obtained. These are salts of disulphaminebenzoic acid, $C_6H_3\begin{cases}COOH\\SO_2NH_2\\SO_2NH_2\end{cases}$. Strong acids throw down from solutions of these salts sulphaminebenzoic sulphinide, and not disulphaminebenzoic acid. The existence of the free acid seems to be improbable, as all attempts to obtain it have failed. The salts of disulphaminebenzoic acid could not be obtained in crystalline form. They all appear strongly hygroscopic, and could not be obtained in a form suitable for analysis. Lead, barium, calcium, potassium and sodium salts were prepared, but with the exception of the calcium salt were not analyzed. The analysis of the calcium salt was undertaken to prove that the salts were disulphaminebenzoates.

The ester, which crystallizes well, was also analyzed with the same object. This latter compound is best adapted for the purpose.

Calcium disulphaminebenzoate, $C_6H_3\begin{cases}COOca\\(SO_2NH_2)_2\end{cases}$, is obtained if a solution of sulphaminebenzoic sulphinide is neutralized with Iceland spar, and the solution evaporated to dryness. The salt appears as a syrupy mass. It loses its water at 120°, and on exposure to the moist air proves to be very hygroscopic. It is very easily soluble in hot and cold water. Alcohol dissolves it less readily, and from this solution it separates in amorphous condition. Ether does not dissolve it. Two calcium determinations were made of this salt, which gave the following data:

I. 0.472 gram of the calcium salt gave 0.109 gram $CaSO_4 = 0.032$ gram Ca.

II. 0.52 gram substance gave 0.12 gram $CaSO_4 = 0.0354$ gram Ca.

The analyzed salt was dried at 120°.

		Calculated.		Found.	
				I.	II.
$C_7H_7S_2N_2O_6$	...	279	93.31	...	...
$Ca\frac{1}{2}$	...	20	6.69	7.00	6.80
		299	100.00		

Disulphaminebenzoic ethyl ester, $C_6H_3\begin{cases}COOC_2H_5\\(SO_2NH_2)_2,\end{cases}$ can be prepared from sulphaminebenzoic sulphinide, alcohol and dry hydrochloric acid in the ordinary way. The alcohol must be as nearly absolute as possible (repeated distillation over caustic lime is sufficient), and the hydrochloric acid must be dried perfectly to effect a complete transformation of sulphaminebenzoic sulphinide into the ester.*

After the alcoholic solution was saturated with hydrochloric acid it was evaporated to dryness. The residue was recrystallized from water, when long, beautiful needles of a silky lustre were obtained, which proved to be the desired ester. The ester is difficultly soluble in cold, more soluble in hot water. Alcohol and ether dissolve it readily. It fuses at 198–200° (uncorr.) On analysis the following results were reached:

I. 0.3146 gram substance gave 0.477 gram $BaSO_4 = 0.0655$ gram S.

* If the same conditions are observed in the case of benzoic sulphinide the ester of orthosulphaminebenzoic acid can be obtained.

II. 0.3105 gram substance gave 26 c. c. N at 27° at 764 mm. barom. = 0.0287624 gram N.

		Calculated.		Found.
$C_9H_{12}O_6$	...	216	70.14	...
S_2	...	64	20.78	20.82
N_2	...	28	9.08	9.26
		308	100.00	

The analyses of the ester and the calcium salt were sufficient to prove that they were derivatives of disulphaminebenzoic acid. It may not be out of place to indicate a possible transformation which the ester, according to analogy, might undergo if subjected to long boiling with dilute hydrochloric acid. As indicated above, in connection with the transformation of $C_6H_3\left\{\begin{matrix}CO\text{—}\\SO_2NH\\SO_2NH_2\end{matrix}\right.$ by dilute hydrochloric acid, one of the ammonia residues (that in the ortho position) can easily be converted into hydroxyl, whereas the other is unaffected by the same treatment. This suggests the possibility of transforming disulphaminebenzoic ester into an acid ester of disulphamine sulphobenzoic acid, with the sulpho-group in the ortho position and the sulphamide group in the para position. Such a transformation could not be well effected otherwise. It is possible that this transformation is not restricted to the group $\left\{\begin{matrix}CO\text{—}\\SO_2NH\end{matrix}\right.$, but that groups like $\left\{\begin{matrix}COOC_2H_5\\SO_2NH_2\end{matrix}\right.$ and $\left\{\begin{matrix}CH_3\\SO_2NH_2\end{matrix}\right.$, in the ortho position with reference to each other, may give similar results.

1, 2, 4 Disulphobenzoic Acid.

If the mother-liquor from sulphäminebenzoic sulphinide is evaporated to a very small volume, potassium chloride separates out. If this operation is repeated until no more potassium chloride is deposited, the last mother-liquor yields a large amount of a well crystallized compound. This was found to contain potassium, but no nitrogen. It is a salt with a remarkable power of crystallization. The analysis of this compound gave the following results:

I. 0.3356 gram substance gave 0.45525 gram $BaSO_4$ = 0.0625 gram S.

II. 0.23655 gram lost 0.0105 gram H_2O at 180°, and gave 0.1093 gram K_2SO_4 = 0.0491 gram K.

	Calculated.		Found.
$C_7H_4O_4$	216.	56.52	...
S_2	64.	17.86	17.73
K_2	78.26	20.84	20.75
H_2O	18.	4.78	4.43
	376.26	100.00	

These figures correspond very closely with those required by a compound of this formula $C_6H_3\begin{cases}COOH\\SO_3OK\\SO_3OK\end{cases} + H_2O$, which is the acid potassium salt of disulphobenzoic acid. Its formation from toluenedisulphamide by oxidation is analogous to that of monopotassium orthosulphobenzoate from tolueneorthosulphamide. It is the same salt which Blomstrand prepared from potassium toluenedisulphonate by oxidation with potassium pyrochromate and sulphuric acid. This is noteworthy, as it can help to explain certain phenomena, noticed in the oxidation of ortho derivatives of toluene, at a later stage of this communication.

Di-potassium disulphobenzoate, $C_6H_3\begin{cases}COOH\\(SO_3OK)_2\end{cases} + H_2O$, crystallizes in large, rhombic forms from its aqueous solution. It is more soluble in hot than in cold water. In cold hydrochloric acid it is less soluble than in water. Alcohol and ether do not act upon it.

The late Dr. J. R. McD. Irby, to whom I am indebted for his kindness in examining the salt crystallographically, gave me the following statement:

System rhombic, a : b : c = 1.3483 : 1 : 1.8288.

Forms—{ 011 }–{ 101 }–{ 001 }–{ 100 }–{ 098 }–{ 1588 }–{ 15823 }.

He had promised to publish certain interesting crystallographical relations which he had found to exist between the acid potassium salt of orthosulphobenzoic acid and the salt here described, but was prevented from doing so by his sudden death.

The proportions in which the nitrogenous acid and the non-nitrogenous potassium salt are formed from toluenedisulphamide by oxidation are very nearly the same as in the oxidation of tolueneorthosulphamide. If it were necessary to express this action by a chemical equation, it would be similar to that given in

an earlier paper* on the oxidation of tolueneorthosulphamide. The products of oxidation were formed in equal quantities.

It is remarkable that a nitrogenous acid potassium salt of the formula $C_6H_3\begin{cases}COOH\\SO_2OK\\SO_2NH_2\end{cases}$ was not formed by the oxidation. At least no trace of a compound containing nitrogen and potassium could be detected. Doubtless, therefore, toluenedisulphamide and tolueneorthosulphamide act in exactly the same way towards potassium permanganate. The sulphamide group in the para position is to some extent influenced by the sulphamide group in the ortho position, at least in the oxidation above referred to. In this special case the result is that both sulphamide groups are converted into sulpho-groups.

In case of toluneparasulphamide, we notice a striking difference. The only sulphamide group present occupies the para position, and it is much more stable than the two sulphamide groups in the compounds just described. This shows that when a second group enters the compound and takes its place in the ortho position, the stability of the former is broken and its conduct towards oxidizing agents changed. I have not prepared many salts of disulphobenzoic acid, since they have been prepared and analyzed by Blomstrand. It has, however, been found that when sulphaminebenzoic sulphinide is heated in a sealed tube with pure hydrochloric acid to 150–170°, it is completely changed into disulphobenzoic acid and ammonium chloride. This furnishes a good method for the preparation of the acid. The solution is then evaporated to dryness, and the residue heated to 200°, in order to volatilize ammonium chloride.

1, 2, 4 Disulphobenzoic acid, $C_6H_3\begin{cases}COOH\\(SO_2OH)_2,\end{cases}$ when recrystallized from pure, concentrated hydrochloric acid, is obtained in large, beautiful crystals, which admit of measurement. The acid is not deliquescent, and can be kept in the air without undergoing any change. It fuses above 285°. On cooling it solidifies to an amorphous, transparent mass. It is very easily soluble in cold as well as hot water. Alcohol and ether do not dissolve the acid. From the pure acid, the acid potassium salt was prepared in the ordinary way, which gave 20.50 per cent. K, the formula $C_6H_3\begin{cases}COOH\\(SO_2OK)_2\end{cases} + H_2O$ requiring 20.78 per cent. K. This

* This Journal, 1, 426.

proved to be identical with the acid potassium salt obtained by direct oxidation from toluenedisulphamide.

In order to prove that when a compound containing the group SO_2Cl and the group COCl in the ortho position with reference to each other is treated with aqueous ammonia, an ammonium salt of a sulphamine acid is formed, the neutral potassium salt of disulphobenzoic acid was subjected first to the action of phosphorus pentachloride. The resulting chloride was then treated with aqueous ammonia, when nothing separated, even after long standing. If the solution be evaporated to a small volume, and be then acidified with hydrochloric acid, sulphaminebenzoic sulphinide is precipitated. Of this the disulphaminebenzoic ethylester was prepared, which fused exactly at 199°. The reaction which takes place in the formation of sulphaminebenzoic sulphinide may be represented thus: First—

$$C_6H_3\begin{Bmatrix}COCl\\SO_2Cl\\SO_2Cl\end{Bmatrix}+6NH_3+H_2O=C_6H_3\begin{Bmatrix}COONH_4\\SO_2NH_2\\SO_2NH_2\end{Bmatrix}+3NH_4Cl.$$

Second: On treating with hydrochloric acid—

$$C_6H_3\begin{Bmatrix}COONH_4\\SO_2NH_2\\SO_2NH_2\end{Bmatrix}+HCl=C_6H_3\begin{Bmatrix}CO\\SO_2NH\\SO_2NH_2\end{Bmatrix}+NH_4Cl+H_2O.$$

Prof. Remsen and Dr. Burney have tried this reaction on other compounds in which the two groups were in the same position, and they have obtained similar results.

Oxidation under varied Conditions.

It was noticed by Remsen and Iles* that when sulphaminemetatoluic acid is oxidized with permanganate of potassium, not sulphamineisophthalic acid, but an acid potassium salt of sulphoisophthalic acid is formed. It was found afterwards by Remsen and Coale† that if the solution is made alkaline, isophthalic sulphinide is obtained as a product of the oxidation. This difference in the result must be ascribed to the fact that in the one case an acid solution is used, while in the other the solution is alkaline. In the acid solution the NH_2 group is replaced by OH, whereas in the alkaline solution this replacement is not effected. The acid solution was

* This Journal, 1, 124. † Ber. d. chem. Ges. 12, 1436.

weak, as the character of sulphaminemetatoluic acid will indicate. It was thought advisable to try the same experiments with toluene-orthosulphamide and 1, 2, 4 toluenedisulphamide, as the two had been shown to conduct themselves in a similar way under the influence of oxidizing agents. For this purpose the above named substances were oxidized in the following ways:

I. *In an acid solution with permanganate of potassium.* This could only be effected by adding an acid to the oxidation mixture, as the two amides under investigation are of an entirely neutral character. Carbonic acid was finally employed for this purpose. It is possible that other acids or acid salts might give the same results. In this special case carbonic acid was conducted for twelve hours through the vessel in which the oxidation was carried on. The heat of a water-bath was constantly applied. The contents were then carefully investigated. It was found that the product of oxidation was in each case not the nitrogenous acid, but the non-nitrogenous potassium salt. After the addition of hydrochloric acid the corresponding acid potassium salts were obtained. No other product was formed.

If, on the other hand, the oxidation is only carried on for three-quarters of an hour under the same conditions as just described, two products are formed; the nitrogenous compound in comparatively small quantity.

II. *In an alkaline solution with permanganate of potassium.* The same proportions of water, permanganate and the substance employed were taken as in the previous experiments. To the solution potassium hydroxide was added. The mixture was then heated on the water bath for four to five hours. The products formed by this oxidation were two in equal quantities, and the same as described before. They did not differ from those obtained by oxidation in a solution neutral at the beginning.

III. *In an acid solution with pyrochromate and sulphuric acid.* The proportions used were: 1 part of toluenedisulphamide, 7 parts of potassium pyrochromate and 10 parts sulphuric acid, diluted with three times its volume of water. After the oxidation had been carried on on the water-bath for five to six hours, it was found that about half of the amide had remained unchanged. It was filtered off. The solution was then reduced with alcohol and treated with barium hydroxide and barium carbonate. The filtrate from the above treatment proved to be strongly alkaline. The solution was evaporated to a small volume, and then hydrochloric acid was

added to it. Nothing was precipitated. This proved the absence of the nitrogenous acid. From the solution, however, a small quantity of acid potassium disulphobenzoate was obtained, which proved to be identical with the salt of Blomstrand, who obtained it by oxidation from potassium toluenedisulphonate, pyrochromate and sulphuric acid. I still think that the large quantity of the unchanged amide in my experiment must have been due to the small quantity of water with which the sulphuric acid was diluted.

From the above experiments the following conclusions can be drawn:

1. That toluenedisulphamide and tolueneorthosulphamide act in the same way towards oxidizing agents.

2. That in an acid solution the products are not the same as those which are formed if the solution is neutral or alkaline at the beginning.

3. That pyrochromate of potassium and sulphuric acid (sufficiently diluted with water) have the same effect on the two sulphamides as permanganate of potassium in an acid solution, but that the yield is much smaller when the former oxidizing agent is employed, and that this must be attributed to certain causes not fully understood at present.

Action of dilute hydrochloric acid on sulphaminebenzoic sulphinide.

If sulphaminebenzoic sulphinide is boiled with dilute hydrochloric acid for four to five hours, complete transformation takes place. If the solution is evaporated by boiling to a very small volume, no trace of sulphaminebenzoic sulphinide is noticed, but a compound of an entirely different nature begins to crystallize out, if the solution is strongly acid.

These first crystals were recrystallized from hydrochloric acid, and subjected to an analysis, which gave the following results:

I. 0.254 gram substance gave 0.4178 gram $BaSO_4$ = 0.0574 gr. S.

II. 0.241 gram substance gave 11 c. c. N at 27° at 766 mm. barom. = 0.012175 gram N.

		Calculated.		Found.
$C_7H_7O_7$	...	202	72.15	...
S_2	...	64	22.85	22.60
N	...	14	5.00	5.05
		280	100.00	

The analysis shows that the compound contains half as much nitrogen and a little less sulphur than the amount required for sulphaminebenzoic sulphinide. All reactions with the compound agree for the formula $C_6H_3\begin{cases}COOH\\SO_2OH\\SO_2NH_2,\end{cases}$ according to which it is sulphamine sulphobenzoic acid, and not sulphobenzoic sulphinide of the formula $C_6H_3\begin{cases}CO\\SO_2NH\\SO_2OH,\end{cases}$ as might have been expected.

Sulphamine sulphobenzoic acid, $C_6H_3\begin{cases}COOH\ (1)\\SO_2OH\ (2)\\SO_2NH_2\ (4)\end{cases}$, crystallizes in large, beautiful crystals. These are not hygroscopic, and can be kept for any length of time in the air without undergoing change. The pure acid fuses at 165° without decomposition. It is so easily soluble in cold as well as hot water that it cannot be well obtained in crystalline form, unless it is left to stand for a very long time in a dessicator over sulphuric acid. It crystallizes well from hydrochloric acid, in which it is not so soluble. The same acid is formed, when the undried, first precipitated sulphaminebenzoic sulphinide is recrystallized from boiling water, as indicated above. Alcohol dissolves it slightly; ether not at all.

To prove in a more direct way that the group SO_2NH, and not the group SO_2NH_2, was changed into the sulpho-group, the following experiment was performed: Two flasks, one of which contained benzoic sulphinide, and the other parasulphaminebenzoic acid in equal quantities, were boiled for several hours with equal volumes of dilute hydrochloric acid. The contents of each flask were then examined. A marked difference was noted between the two: benzoic sulphinide was completely converted into orthosulphobenzoic acid, whereas parasulphaminebenzoic acid remained perfectly unchanged. This strengthens the proof for the correctness of the formula accepted above for sulphamine sulphobenzoic acid.

Attention was called above to the possible transformation of SO_2NH_2 (in the ortho position) into SO_2OH. The further discussion of this subject can be omitted here.

Mono-potassium sulphamine-sulphobenzoate, $C_6H_3\begin{cases}COOH\\SO_2OK\\SO_2NH_2,\end{cases}$ can be obtained, if the free acid is converted into the neutral potassium

salt and this salt be treated with hydrochloric acid in excess. The first two crops of crystals are potassium chloride. On further evaporation, beautiful, transparent crystals, apparently of the rhombic system, were deposited. These contained potassium and nitrogen. They must, however, have undergone a partial decomposition, as the analysis did not agree well for a pure mono-potassium sulphaminesulphobenzoate. The salt was recrystallized several times from strong hydrochloric acid, and after each recrystallization analyzed with the following results:

I. 0.215 gram gave 0.0465 gram K_2SO_4 = 0.0208 gram K.
II. 0.2278 gram gave 0.05 gram K_2SO_4 = 0.0224 gram K.
III. 0.3015 gram gave 0.0693 gram K_2SO_4 = 0.03112 gram K.
IV. 0.2913 gram gave 0.0708 gram K_2SO_4 = 0.0318 gram K.
V. 0.3124 gram substance gave 13.5 c. c. N, at 24°, at 767 mm. barom. = 0.015125 gram N.

	Calculated.		Found.				
			I.	II.	III.	IV.	V.
$C_7H_6O_7S_2$ ...	266.	83.37	...	...	...	...	...
N ...	14.	4.38	...	...	...	...	4.84
K ...	39.13	12.25	9.67	9.83	10.32	10.91	
	319.13	100.00					

From the above analyses it appears that the substance is a mixture of the free acid and the acid potassium salt. It is very probable that the strong hydrochloric acid has effected a partial replacement of both potassium atoms by hydrogen. At all events this seems to be the most plausible explanation. The determinations of potassium and nitrogen confirm this view. The substance was not recrystallized from pure water, in which it is very soluble. A quantity of this salt is still in my possession, and I shall try to purify it, if possible, by recrystallization from water. The impure, air-dried salt fuses at about 300° without loss of weight. It is not soluble in alcohol.

Action of Potassium Hydroxide on 1, 2, 4 Disulphobenzoic Acid.

Blomstrand is responsible for the statement that potassium disulphobenzoate yields, upon fusion with caustic potash at a high temperature, only dioxybenzoic acid. This is not correct. If the fusion is conducted at a temperature above 250° for a considerable

length of time the product is resorcin, and not dioxybenzoic acid; at least no trace of such an acid could be found in the fused mass. The fused mass assumes a deeply carmine red color above 250°, which is the best indication that resorcin has been formed. On dissolving and acidifying the product of fusion, ether extracted a slightly dark colored product. This proved to be very soluble in cold water. Dioxybenzoic acid is, according to Blomstrand's own statement, difficultly soluble in cold water. It could not have been the same product. The product had no acid properties. It was treated subsequently with potassium carbonate in order to remove every possible trace of an acid, and was then extracted with ether for a second time. This second ethereal extract yielded nearly pure resorcin. It crystallized well. It was sublimed, and in this condition it fused at 105° (uncorr.) It gave the characteristic blue reaction with ferric chloride. From it and phthalic anhydride, fluorescein and tetrabromfluorescein were obtained. These reactions were sufficient to identify it. The residue from the second ethereal extract was acidified with hydrochloric acid, and for a third time extracted with ether. On this occasion, however, ether extracted nothing, showing that the expected dioxybenzoic acid was not a product of this particular fusion.

Dioxybenzoic acid can be easily prepared from potassium disulphobenzoate, if the fusion is conducted at a moderate temperature, not exceeding 250°. It must be remembered that the slightest change in color is an indication of a decomposition of dioxybenzoic acid into resorcin and carbonic acid, and that this should be avoided if a large yield of the acid is the object of the fusion. It is very difficult to avoid the formation of a small quantity of resorcin. The fused mass has to be treated in the way indicated above. The first extract contains resorcin and dioxybenzoic acid together. The second, after treatment with potassium carbonate, resorcin, and the third dioxybenzoic acid, with all the characteristic properties ascribed to it by Blomstrand. It crystallizes with $1\frac{1}{2}$ molecules of water, one of which it loses in the air. The amount of water found in the acid, which was dried in the air, was 5.58 per cent. H_2O. The formula $C_6H_3\begin{cases}COOH\\(OH)_2\end{cases} + \frac{1}{2}H_2O$ requires 5.52 per cent. H_2O. Pressed between filter paper and then analyzed, it gave 14.94 per cent. H_2O. The formula $C_6H_3\begin{cases}COOH\\(OH)_2\end{cases} + 1\frac{1}{2}H_2O$ requires 14.92

per cent. H_2O. Blomstrand states that it crystallizes from hot water with ½ a molecule of water, and from cold water with 2½ molecules of water. I find that it always contains 1½ molecules when it is pressed between filter paper, and ½ a molecule when it is dried in the air. It is very difficult to account for the difference in the water of crystallization unless we assume a typographical error in B.'s statement. He certainly did not notice the fact that the acid loses its water of crystallization at ordinary temperatures.

1, 2, 4 Dioxybenzoic acid, $C_6H_3\begin{cases}COOH\\(OH)_2\end{cases} + 1\frac{1}{2}H_2O$, crystallizes from water in beautiful, long needles. It fuses at 194° (uncorr.). The same fusing point was noticed if the acid was first dried at 120°. It is very easily soluble in hot water, but very difficultly soluble in cold water. Its hot, saturated solution solidifies on cooling. Alcohol and ether dissolve it readily. With ferric chloride it gives a characteristic dark red color. Dioxybenzoic acid is transformed at its fusing point into resorcin and carbonic acid. On fusion with caustic potash this transformation takes place at a slightly higher temperature, but the exact temperature was not determined. This is one of the few cases in which a carboxyl group is replaced by hydrogen on fusion with potassium hydroxide.

I shall take up the study of the salts and of the different esters of 1, 2, 4 dioxybenzoic acid at the first opportunity.

The formation of resorcin escaped Blomstrand's observation, or else the structure of dioxybenzoic acid would have been determined. It not only proves now the structure of dioxybenzoic acid, but also that of all the derivatives of *a*-toluenedisulphonic acid. Four dioxybenzoic acids are known; of these, this is the third of which the structure has been determined. The three dioxybenzoic acids, the structures of which are known, are given below:

Names of the Acids.	Yielding	Position of Groups.		
Oxysalicylic acid	Hydroquinone	1	2	5
Protecatechuic acid	Pyrocatechin	1	3	4
1, 2, 4 Dioxybenzoic acid	Resorcin	1	2	4

The position of the carboxyl group is indicated by 1.

The fourth dioxybenzoic acid is the acid prepared by Barth and Senhofer.* Of this it can only be said that the groups are, in all probability, located in the positions 1, 3 and 5, though experi-

* Liebig's Ann. 159, 222.

mental proof has not been given up to the present. Resorcin and dioxybenzoic acid have been prepared by fusion with potassium hydroxide, from disulphobenzoic acid, sulphaminebenzoic sulphinide and sulphaminesulphobenzoic acid.

Toluenedisulphonic acid conducts itself in a different manner when fused with caustic potash. It yields: 1. Salicylic acid; 2. Paraoxybenzoic acid; 3. 1, 2, 4 Dioxybenzoic acid (in very small quantity); 4. 1, 2, 4 Isorcin; 5. Resorcin. The two last named substances could not be well separated from each other, but the presence of resorcin was detected by the fluorescein reaction with phthalic anhydride. It was, however, found that a second compound must have been present which differed in some respects from resorcin; as fluorescein was not the only product formed in the reaction with phthalic anhydride. This might have been the 1, 2, 4 isorcin of Senhofer and Blomstrand, but this cannot be said with certainty, as there is no proof of the fact.

The structure of α-toluenedisulphonic acid is proved by the following facts:

I. *Toluneparasulphochloride* and *tolueneorthosulphochloride* yield *only one and the same toluenedisulphonic acid*, upon treatment with fuming sulphuric acid at temperatures not exceeding 150°.

II. Toluenedisulphamide yields by oxidation a *sulphinide*, which indicates that the CH_3 group and one SO_2NH_2 group are in the ortho position with reference to each other.

III. The relative position of the two sulpho-groups with reference to each other is determined by the *formation of resorcin* from all products of oxidation of toluenedisulphonic acid.

According to the above proofs the groups in toluenedisulphonic acid and its derivatives *are in the positions 1, 2 and 4.*

BALTIMORE, *June*, 1880.

REVIEWS AND REPORTS.

Report on the Progress of Analytical Chemistry.

(*Continued from p.* 76.)

Hydrogen Dioxide.—A. Bertrand,* "On the volumetric Determination of active Oxygen in Barium and Hydrogen Dioxides." The method is based on the following reactions:

1. $BaO_2 + 2HCl = BaCl_2 + H_2O_2$.
2. $H_2O_2 + 2KI = K_2O + H_2O + I_2$.
3. $2Na_2S_2O_3 + I_2 = 2NaI + Na_2S_4O_6$.

Chlorine.—G. Vortmann,† "Detection and Determination of Chlorine in the Presence of Bromine and Iodine." In the presence of acetic acid iodides are completely decomposed by the superoxides of lead and manganese. The former oxidizes a part of the liberated iodine to iodic acid, but not the latter. Bromides in neutral solutions are not decomposed by either oxide, and in solutions acidified with acetic acid only by the lead compound. Chlorides are not attacked by either oxide in the presence of acetic acid. Therefore, to detect chlorine in the presence of bromine and iodine, it is recommended to treat the solution with acetic acid and lead superoxide, and to boil until the solution remains colorless on clearing and no longer smells of either bromine or iodine. The bromine and a part of the iodine will have been expelled, while a portion of the latter will remain behind as iodate of lead. On filtering and washing with hot water, the whole of the chlorine free from bromine and iodine will be obtained in the filtrate.

Iodine.—E. Donath,‡ "On a new Method of detecting and determining Iodine in the Presence of Chlorine and Bromine." Chromic acid liberates iodine from its compounds with the alkalies, but does not decompose the corresponding chlorides and bromides. The iodine thus liberated may be removed by distillation and determined in the distillate. If bromides are present the distillation must be interrupted as soon as the vapors of iodine cease to pass over, since they are to some extent decomposed when the solution becomes concentrated by evaporation.

Sulphur.—R. Fresenius,§ "On the Determination of the Sulphur of Pyrites." The sulphur of a specimen was determined by three different persons, according to the method recommended by Fresenius,‖ which consists in fusing the finely pulverized material with a mixture of a nitrate and a carbonate of an alkali. The mean of

* Bull. de la Soc. Chim. 33, 148. † Berichte, 1880, 325. ‡ Z. an. Ch. 19, 19.
§ Z. an. Ch. 19, 53. ‖ Z. an. Ch. 16, 339.

the results obtained was 43.87 per cent. The sulphur of the same specimen was then determined by the method recommended by Lunge,* which consists in the oxidation of the material by a mixture of one part of fuming hydrochloric acid and three or four parts of nitric acid having a specific gravity of 1.36 to 1.4, evaporation with hydrochloric acid until all nitric acid is expelled, treatment of the residue with a little hydrochloric acid, filtration, precipitation of the sulphuric acid from the boiling solution with a boiling solution of barium chloride, immediate decantation through the filter, and washing—at first by decantation and with addition of a few drops of hydrochloric acid. The mean of the results thus obtained was 42.61 per cent. On heating the barium sulphate became red, and quantities of ferric oxide varying from 0.004 to 0.0085 gram were extracted. Notwithstanding the presence of the iron, the precipitates were considerably too light. On searching for the causes of the discrepancy in the results obtained by the two methods, it was found that the sulphuric acid is not completely precipitated at first when hot solutions of it, containing hydrochloric acid, are treated with a barium salt. The quantity not immediately precipitated is considerable, and greater in proportion to the amount of hydrochloric acid present. Moreover, the presence of ferric chloride hinders the precipitation.

Phosphorus.— Brunner,† "Determination of assimilable Phosphoric Acid according to Petermann." A description of the method employed by Petermann for the simultaneous determination of soluble and reverted phosphoric acid in commercial fertilizers. An appropriate weight of the material, varying from ten to two grams according as the quantity of phosphoric acid is small or large, is washed into a porcelain mortar with a solution of citrate of ammonium having a specific gravity of 1.09, gently rubbed, the suspended matter gradually poured into a 500 c.c. measuring flask, and the residue finally washed in with the citrate solution until 100 c.c. have been used. The flask is then heated exactly one hour at 35°, filled to the mark, and the contents filtered. In a measured quantity of the clear portion of the filtrate the phosphoric acid is precipitated by chloride of magnesium and ammonia, and determined as pyrophosphate of magnesium. The method yields concordant and fairly correct results.

C. Mohr,‡ "A volumetric Method of determining Phosphoric Acid in crude Phosphates and Superphosphates with Uranium in the presence of Ferric Oxide." The author proposes the following modified uranium method: From two to five grams of the finely ground material are dissolved in the heat by frequently renewed small quantities of dilute nitric acid. The several portions of liquid thus obtained are united, diluted to a known volume and filtered. A measured quantity of the filtrate is treated with acetate of sodium until a persistent turbidity is obtained, after which a quantity of the uranium solution is allowed to flow in, the liquid heated to boiling,

* Handb. der Soda-Fabrication, 1, 92. † Z. an. Ch. 19, 141. ‡ Z. an. Ch. 19, 150.

and treated, before the complete precipitation of the phosphoric acid has been effected, with a few small grains of ferrocyanide of potassium. The phosphate of iron is decomposed with formation of Prussian blue. Care must be taken not to add too much of the ferrocyanide of potassium. Enough has been added when a drop of the liquid no longer gives the iron reaction.

Arsenic.—E. Donath,* "On the Decomposition of Compounds containing Arsenic and Antimony." These are frequently fused with carbonate of sodium and sulphur, and the soluble arsenic and antimony compounds thus produced extracted with water. The objection to the method lies in the fact that a large quantity of soluble sulphides is produced which, on being acidified, deposit sulphur. This difficulty may be wholly obviated by fusing with hyposulphite of sodium instead of the mixture mentioned. The hyposulphite should be previously thoroughly dehydrated and pulverized.

Potassium.—F. Muck,† "On the Removal of large Quantities of Potassium and Sodium Chlorides in Mineral Analyses." For this purpose advantage is taken of their insolubility in concentrated hydrochloric acid.

A. Van Hasselt,‡ "The direct Determination of the Soda contained in Potash." The method consists in converting the carbonates into chlorides, and extracting the chloride of potassium by means of strong hydrochloric acid saturated with the chloride of sodium.

Zinc.—V. Drewsen,§ "A new Method of determining the Value of Zinc Dust." The method consists in ascertaining how much bichromate of potassium the material will reduce in the presence of dilute sulphuric acid.

Cerium.— F. Stolba,‖ "The volumetric Determination of Cerium." This metal may be quantitatively determined by means of potassium oxalate and potassium permanganate in exactly the same manner as calcium.

Nickel.—G. Papasogli,¶ "Detection of Nickel in the Presence of Cobalt." If a small quantity of a salt of nickel is dissolved in cyanide of potassium and a strip of zinc brought into the solution, gas is evolved, the zinc becomes covered with a black deposit and the solution in its vicinity changes to a red color. Cobalt does not give this reaction, nor does its presence prevent it. If the platinum electrodes of a Bunsen's element are brought into a solution of potassium-nickel cyanide the same reaction appears at the negative pole. It cannot, however, be obtained by simply passing hydrogen through the solution.

Cobalt.—C. Rössler,** "A new Method of determining Manganese and Cobalt volumetrically." A more detailed account of the method reported in this Journal, Vol. I. page 363. The author finds that the method is applicable to the determination of cobalt

*Z. an. Ch. 19, 23. †Ibid. 19, 140. ‡Ibid. 19, 156. §Ibid. 19, 50.
‖Chem. News, 41, 31. ¶Berichte, 1880, 203. **Liebig's Ann. 200, 323.

as well as manganese. In the presence of nickel however, the results obtained are somewhat too low.

Iron.—J. M. Eder,* "A new Method for the Quantitative Determination of Ferrous Oxide in the Presence of Organic Acids and Cane Sugar." If a solution of potassium ferro-oxalate is treated with an excess of silver nitrate, it is completely converted into a ferric salt while a corresponding amount of metallic silver separates out. Moreover, when a ferrous salt, whether organic or inorganic, in a solution free from mineral acid is treated with neutral oxalate of potassium, the potassium ferro-oxalate is formed, and on addition of silver nitrate the reaction just described takes place according to the following equation: $2FeO + Ag_2O = Fe_2O_3 + 2Ag$. Each atom of silver precipitated represents one atom of ferrous iron. All of the compounds except ferric hydroxide, which separate out with the silver can be removed by means of ammonia. The silver may then be dissolved in nitric acid and precipitated as chloride. It sometimes happens that the metallic silver does not readily subside. In such cases ammonia and afterwards chloride of ammonium are to be added. If a sufficient quantity of tartaric acid is present iron is not precipitated by the ammonia, and the silver may be collected and weighed as such. The best method of procedure is the following: The nearly neutral solution of ferrous salt is treated with an excess of potassium oxalate and silver nitrate and allowed to stand for some minutes. Tartaric acid sufficient to prevent the precipitation of iron is then added and finally an excess of ammonia. The precipitate of metallic silver is collected upon a filter and washed with a solution of ammonia and chloride of ammonium. Care should be taken to avoid a strong light.

Lead.—F. Lux,† "Volumetric Determination of the Value of Minium." Lead superoxide when treated with an excess of oxalic acid undergoes decomposition as follows:

$$PbO_2 + C_2H_2O_4 = PbO + 2CO_2 + H_2O.$$

The oxalate of lead formed by the union of the excess of oxalic acid with the reduced oxide dissolves readily in dilute nitric acid, and in this solution the undecomposed oxalic acid may be easily determined by means of permanganate of potassium. This method combined with the volumetric determination of lead by means of potassium bichromate, affords a rapid and sufficiently accurate means of ascertaining the commercial value of minium.

Alcoholic Liquors.—V. Wartha,‡ "Contributions to the Investigation of Wine." This article treats of the detection of rosaniline compounds and of the detection and determination of sulphurous acid in wine.

L. Weigert,§ "Detection of Salicylic Acid in Wine, &c." K. Portele proposed the following method for highly colored liquids: 100 to 200 c. c. of the fluid are treated with a solution of glue in order to precipitate the tannic acid, and then, without removing

* Berichte, 1880, 502. † Z. an. Ch. 19, 153. ‡ Berichte, 1880, 657.
§ Z. an. Chem. 19, 45.

the suspended matter, evaporated to dryness on the water-bath. From the residue the salicylic acid is extracted with ether, the extract evaporated, the acid dissolved in water and tested for with ferric chloride. In this manner one gram of the acid dissolved in a hectoliter of liquid can be detected. The author proposes as an improvement on this the following method: 50 c. c. of the material to be examined are agitated for some minutes with 5 c. c. of amyl alcohol; the alcohol, which rises to the top, is drawn off and dissolved in an equal volume of ethyl alcohol. The solution thus obtained is tested with ferric chloride.

Butter.— L. Medicus and S. Scherer,* "On the Testing of Butter." The authors commend on the basis of their own experiments the method of Reichert,† which involves the alkalimetric determination of the volatile fatty acids. They also find that melted butter does not solidify to a perfectly homogeneous mass on cooling, and that there is therefore need of some care in selecting an average specimen when butter which has been melted (Butterschmalz) is to be examined for adulteration.

Carbohydrates.—F. Soxhlet,‡ "The Conduct of Sugars towards Alkaline Copper and Mercury Solutions." The author has given in considerable detail the results of an extended and carefully conducted examination of Fehling's, Knapp's and Sachsse's methods for determining sugar. The three were investigated with reference to their application to inverted cane, grape and milk sugars, also lactose and maltose. His conclusions are, in general, 1. that each of these substances has a different reducing power for Fehling's solution; 2. that the relation between copper reduced and sugar decomposed is not constant, but depends on the concentration of the solutions and on the amount of copper in solution, or perhaps on both of these factors at the same time; 3. that the methods of Knapp and Sachsse have no advantages over that of Fehling in respect to accuracy, certainty or convenience.

Alizarine, &c.—E. Schunck and H. Roemer,§ "On the Detection of Alizarine, Isopurpurine and Flavopurpurine." These three substances give such characteristic reactions that their separate detection is a matter of no difficulty. The opposite is true when they occur as mixtures. A complete separation is very difficult, and impossible with small quantities of material. The reason of this lies in the similar conduct of all three towards most solvents, and in the fact that the characteristic reactions are in the main those of color. The separation can, however, be effected by means of fractional sublimation, that of alizarine from the other two quantitatively and with ease, that of isopurpurine from flavopurpurine with greater difficulty. Alizarine begins to sublime at 110°, flavopurpurine at 160°, and isopurpurine at 170°. The last two may be easily identified in the sublimate; since isopurpurine sublimes in the form of stout and quite perfect crystals, which appear to

* Z. an. Chem. 19, 159. † Ibid. 18, 68. ‡ Jour. f. pr. Ch. 21, 227.
§ Berichte, 1880, 41.

belong to the rhombic system; flavopurpurine, on the other hand, in the form of reddish-yellow needles. Moreover, the two may be separated by means of benzene, in which the former is nearly insoluble and the latter quite soluble. The apparatus used consists of two glass plates separated by a ring of lead a few millimeters in thickness.

Urea.—E. Pflüger,* "On the Quantitative Determination of Urea." The quantity of urea obtained by Liebig's method, as usually conducted, is too small. This defect may be remedied by adding at once nearly the whole amount of the nitrate of mercury required by the urea, neutralizing, and finally adding enough more of the mercury solution to give the end reaction. The author also finds it necessary to alter somewhat the correction proposed by Liebig for solutions containing less than 2 per cent. of urea.

A. Fauconnier,† "On the Determination of Urea by Alkaline Hypobromites and Hypochlorites." In view of the dispute between Méhu and Esbach with reference to the influence of sugars on the liberation of nitrogen from urea by these reagents, experiments were made upon standard solutions of urea, two of which contained a known quantity of grape sugar, and a third a known quantity of cane sugar. From the solutions containing the grape sugar very nearly the theoretical amount of nitrogen was obtained, while in the case of that containing the cane sugar there was the usual deficit. The author concludes, from some experiments made by him, that the $\frac{3}{4}$ of nitrogen not liberated when urea is treated with hypobromite undergoes oxidation to nitric acid, and that grape sugar is able to reduce this with liberation of the nitrogen.

Jay‡ finds, on the contrary, that the presence of cane sugar does increase the volume of gas liberated; though, in order to obtain the theoretical amount it would be necessary to add a quantity of the sugar equal to about two hundred and sixty-five times that of the urea. No gas is evolved during the time ordinarily required for a determination of urea when a solution of pure cane sugar is treated with hypobromite, yet the author does not believe that the additional quantity of gas obtained when this sugar is present in the solution of urea is due to a more complete liberation of nitrogen.

H. N. MORSE.

REPORT ON PROGRESS IN PHYSIOLOGICAL CHEMISTRY.

The science of physiological chemistry treats of the chemistry of the body. It is not merely a description of the proximate principles composing the different tissues and fluids of the body, but includes the more important study of the chemical processes and chemical changes taking place during life; it is the development of events by chemical processes in the body. But the more elevated bio-chemistry is dependent in great part upon the facts of zoo-

* Berichte, 1880, 780. † Bulletin de la Soc. Chim. 33, 102. ‡ Bulletin, 33, 105.

chemistry for its theories. Before we can understand the action of any particular substance in the body we must know its composition, and in order to understand its relation to some more complex substance from which it may possibly be derived we must know its constitution. The science of organic chemistry in its rapid development has taught us much of the constitution of complex organic matter, and it is in this manner that physiological chemistry derives most benefit from zoo-chemistry. By means of the facts which it teaches we are enabled to trace to a common origin many simple bodies resulting from chemical metamorphosis in the body, and so of late much time has been spent in studying certain forms of organic matter of special importance physiologically, in order to better understand their breakings up in the animal body.

Within the past few years the decomposition of albumin under varying conditions, and by the agency of different chemical agents, has been carried on extensively in the hope of ascertaining something in regard to the constitution of this complex substance. Of great importance chemically and physiologically, it has long resisted the efforts of investigators to unravel its complicated structure, and physiologists have long been puzzled to account for the many and diverse forms of decomposition-products resulting from its splitting up in the animal body. Not yet can we consider the matter thoroughly understood, but the investigations of the past few years have thrown so much light upon the subject that our knowledge is considerably broadened.

It has been a prevalent opinion that the albuminous substances must stand somewhat intimately related to the carbohydrates, on account of the fact that the products of fermentation or decomposition of both substances were found to be closely related if not identical; and when it was discovered that by the action of bromine on glucose,* dextrin, and other carbohydrates, new and peculiar bodies having the properties of acids were formed, a way appeared to be opened for the solution of the problem of the chemical relationship of the albumins and carbohydrates. Thus, in 1871, Hlasiwetz and J. Habermann† undertook, by a series of qualitative and quantitative experiments, to ascertain if it were possible by the oxidation of different forms of albumin with bromine to obtain the peculiar acids formed by the oxidation of glucose and dextrin under similar circumstances, viz: gluconic and dextronic acids. Egg-albumin, casein and other forms of albumin decomposed by heating in a closed vessel with bromine, all agreed in giving aspartic, oxalic and carbonic acids, together with leucin and a considerable quantity of brominated compounds, but no trace of gluconic, dextronic or glycollic acids were obtained, and strange to say no tyrosin was found. Thus these investigators were not able to find direct proof of the pre-existence of carbohydrates in the albuminous matters as would have been evidenced by the finding of gluconic or other allied acid.

* Annalen der Chem. u. Pharm. 155, 1; 162, 297. † Ibid. 159, 304.

Still imbued with the idea of a probable relationship between the two classes of matter, they accounted for the absence of gluconic acid by the readiness of its decomposition into carbonic, oxalic and bromacetic acids, together with bromoform; while the absence of tyrosin was accounted for on the strength of Städeler's statement that tyrosin, by the action of chlorine, is completely changed into chloranil and chloracetone, so that it would apparently follow that bromine would act in the same manner with formation of bromanil and bromacetic acid; both of which were found, the latter in considerable quantity. Thus their decomposition of albuminous matter in this manner, though failing in the desired object, showed the presence of bodies which arranged themselves naturally into two well defined groups, the fatty and aromatic; as had also been found by investigators preceding them, but using different methods of oxidation; while a glance at the individual bodies formed shows that the highest members contain not more than six atoms of carbon in the principal radical—leucin $C_5H_{10}\begin{cases}NH_2\\COOH.\end{cases}$

Thinking that a more careful oxidation might show the wished for bodies, Hlasiwetz and Habermann* in 1873 tried another series of experiments, using in one case hydrochloric acid and zinc chloride as the decomposing agent, and in another case dilute sulphuric acid. But in these experiments likewise they failed to find the characteristic acids formed by the oxidation of carbohydrates, obtaining simply the remote decomposition-products acetic acid, oxalic acid, etc., which, together with other bodies formed, are likewise products of the decomposition of carbohydrates. As nearer decomposition products, however, by hydrochloric acid and zinc chloride, they obtained from casein, aspartic acid, the previously discovered (by Ritthausen) glutamic acid, also leucin, tyrosin, together with some phosphoric acid, sulphuric acid and always ammonium chloride, likewise a new hydrochloric acid compound of glutamic acid, but no trace of sugar-like bodies was found nor characteristic derivatives of the same. Thus according to these authors' conclusions certain nearest or primary decomposition-products are always formed, and then besides a whole series of similar ones which are secondary, so that as characteristic for albuminous matter we have only the highest members, leucin, tyrosin, aspartic acid and glutamic acid: all the remaining are products common to both albumin and carbohydrates, and when formed from albumin may be considered as descendants of the higher members, leucin, tyrosin, etc. So the old theory of the relationship of these two classes of matter has apparently received its death-blow by these carefully conducted experiments, and although later investigators have obtained in the oxidation of albuminous matter peculiar sugar-like bodies, still nothing has been brought forward to overthrow the now generally accepted belief in the independent position of the albumins and carbohydrates.

*Annalen der Chem. u. Pharm. 169, 150.

In 1875 Schützenberger* commenced a series of investigations upon the chemical constitution of albuminous matter, and the importance of his results is in great part dependent upon the fact that he was able to obtain a complete decomposition of the albumin, and also on his careful determination of the quantities of the different decomposition-products. He also tried the action of boiling dilute sulphuric acid on albumin with entirely new results. The plan of procedure in this latter case was to take a portion of moist coagulated albumin corresponding to one kilogram of the dry substance, mixing this with about 8 litres of water containing 200 grams of concentrated sulphuric acid, and boiling the mixture during 1½ to 2 hours; at the end of which time the mass was cooled and filtered, the residue being washed thoroughly with water until the washings were no longer acid.

The insoluble portion appears much like silicic acid or alumina, being white in color, flocculent and homogeneous, and on being dried is found to weigh always about one half the original amount. When dried it is devoid of taste, slightly yellow in color, with very weak acid reaction, insoluble in water, alcohol and ether. Thus it is found that boiling dilute sulphuric acid resolves the albumin molecule into two equal parts, of which one is soluble and the other insoluble. The insoluble portion so prepared is called hemiprotein, a substance which combines with acids and bases, forming soluble compounds, and can be purified by solution in soda, reprecipitated by exact neutralization with hydrochloric acid and washed thoroughly with water and alcohol. Prepared in this manner it contains a small quantity of sulphur, but on combustion does not leave even a trace of ash, and dried at 110° gives as an average result C 53.60, H 7.19, N 14.45 per cent. Hemiprotein boiled a longer time with dilute sulphuric acid passes slowly into solution with formation of a new substance, which is amorphous but of a slightly sweet taste, soluble in water and alcohol. This substance, called hemiproteidin, formed from hemiprotein together with leucin, tyrosin, and their homologues, gives by analysis results which lead to the empirical formula $C_{24}H_{42}N_6O_{12} + H_2O$.

The original sulphuric acid solution filtered from the hemiprotein, and containing matter corresponding to the second half of the original albumin, contains a large proportion of an amorphous substance called hemialbumin, of a very weak acid reaction, and giving by analysis the formula $C_{24}H_{40}N_6O_{10}$. Hemialbumin makes up by weight the greater part of the substances isolated from the sulphuric acid solution, and its relation to hemiproteidin is shown by the following formulae:

$$C_{24}H_{40}N_6O_{10} + O + H_2O = C_{24}H_{42}N_6O_{12}.$$

In the sulphuric acid solution was also found an acid precipitated by lead acetate and having the formula $C_{24}H_{40}N_6O_{16}$, also a body free from nitrogen, which reduced Fehling's solution vigorously,

* Bulletin de la Société chimique de Paris, 1875-76.

and which is probably glucose or a similar body, also another body which had all the properties of sarkin.

Schützenberger has, however, obtained a more complete decomposition of albumin by boiling with barium hydroxide. He first observed that moist coagulated albumin treated with a solution of barium hydroxide in the cold was gradually dissolved and finally evolved ammonia, and that if the mixture was heated, the solution took place more rapidly with an abundant evolution of ammonia, and that, finally, the clear solution gave a granular precipitate consisting principally of barium carbonate. He found that even 120 hours' boiling of the albumin with barium hydroxide was not sufficient to break up the albumin molecule completely. As products of such a partial decomposition, however, he found, together with a large quantity of crystalline substances, a non-crystalline body, which in its reactions and composition was similar to hemiproteidin, and this substance heated to 150° with barium hydroxide decomposed in its turn with formation of carbonic acid and ammonia. In order to obtain a complete decomposition it was necessary to heat the albumin in a sealed iron flask at 150–200° for 4–6 days. By heating for a shorter time intermediate products were obtained, and these by longer treatment were converted into simple compounds.

Thus in three different experiments where albumin was heated 120 hours at 100°, 24 hours at 150°, and 8 days at 150°, with barium hydroxide, a row of decomposition-products, partly old and partly new, were obtained, and by a careful determination of their quantity much that is of importance has been learned.

By a determination of the nitrogen evolved as ammonia by heating with barium hydroxide solution, it was found that similar kinds of albumin yielded a corresponding amount; thus blood-, muscle- and plant-albumin furnished 4.3–4.8 per cent. N, egg- and serum-albumin 3.9–4 per cent. N, casein and hemiprotein 3.5–3.6 per cent. N, while ossein and gelatin yielded only 2.55–3.00 per cent. N. An examination of the precipitate obtained by heating albumin with barium hydroxide as in the previous cases, revealed the presence of carbonic, oxalic and sulphurous acids, and occasionally when the albumin was not quite free from fat, baryta soap. It is a noticeable fact that the proportion by weight of the free obtained nitrogen stands very close to the thrown off carbonic and oxalic acids, and according to Schützenberger's views, the carbonic acid and ammonia may originate from the decomposition of urea and oxamide, these two groups presumably being contained in the albumin molecule. Thus from 100 grams of casein were obtained,

17.5 grams $BaCO_3$
7.6 " BaC_2O_4

25.1

Nitrogen corresponding to the oxalate calculated according to the decomposition equation of oxamide is 2.17, and nitrogen cor-

responding to the carbonate calculated according to the decomposition equation of urea is 1.08. Total nitrogen calculated for the 25.1 grams of precipitate is thus 3.25, while the nitrogen found was 3.54, making a difference of only .29. A number of similar experiments with different kinds of albumin all gave the same results. While the results thus show that the relation of the nitrogen to the baryta precipitate is a constant one, the experiments also show that the composition of the baryta precipitate in regard to the proportion of oxalate to carbonate is very variable. This fact is explained by the theory that the oxamide group $C_2O_2\begin{cases}NH_2\\NH_2\end{cases}$ may represent in part the urea group $CO\begin{cases}NH_2\\NH_2\end{cases}$ similarly as in feldspar the alkali metals mutually represent or replace each other in variable proportion, or by the theory that the albumin is made up of two albuminous bodies, of which one may be a derivative of urea, the other of oxamide, the two being united in variable proportion.

While the quantities of acetic acid formed from the different kinds of albumin were found to be quite close in their agreement, tyrosin was found in widely differing quantities.

	Grams.
Tyrosin formed from 100 parts albumin,	2.03
" " casein,	4.12
" " hemiprotein,	2.20
" " blood-fibrin,	3.20
" " plant-fibrin,	2.00

In addition to tyrosin, leucin, etc., a number of new bodies hitherto unknown as decomposition-products of albumin were discovered, viz.: crystalline amido-acids of the general formula $C_nH_{2n}NO_2$, butalamine, alanin, amidovalerianic acid; 2dly, amido-acids of the aspartic acid series $C_nH_{2n} - NO_4$. In addition to aspartic acid and glutamic acid, $C_5H_9NO_4$, a monobasic amido-acid crystallizing in glistening prisms, was found having the formula $C_5H_7NO_3$, and called glutimic acid; a body of quite interesting properties, but formed only in small quantity, 1 kilo. albumin yielding but 1.5–2 grams. Several crystalline bodies having a sweet taste were found in considerable quantity, and from their peculiar properties were called leucein and *a* and *b* gluco-protein. These three bodies differ from the amido-acids of the series $C_nH_{2n} + NO_3$, simply through a smaller content of hydrogen, and appear to be compounds of leucin or its homologues with amido-acids, poor in hydrogen, as is evidenced by the action of dilute sulphuric acid, which forms from either of these bodies sulphate of leucin and an acid of the acrylic acid series. In this case also, as in the decomposition of albumin with dilute sulphuric acid, a small quantity of non-nitrogenous substances similar to dextrin and glucose was obtained.

Schützenberger finally arrives at the conclusion that albumin is a complex ureid which contains about one-fifth of its nitrogen in the

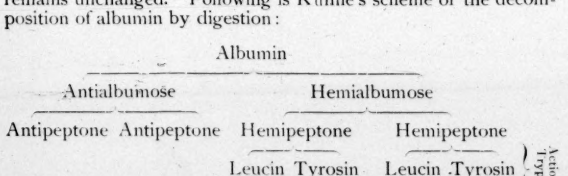
form of urea, and that in the decomposition of albumin with barium hydroxide the albumin molecule $C_{72}H_{112}N_{18}O_{22}S$ loses two molecules of urea, one molecule of acetic acid, one atom of sulphur, and takes up sixteen molecules of water.

$$C_{72}H_{112}N_{18}O_{22}S + 16H_2O = 2CN_2H_4O + C_2H_4O_2 + C_{68}H_{102}N_{14}O_{34} + S.$$

The formula $C_{68}H_{102}N_{14}O_{34}$ can be decomposed as follows: Into three molecules of glutamic or aspartic acid, which quantity actually corresponds to the baryta not precipitated by carbonic acid; and secondly, into a mixture of equal molecules of amido-acid of the composition $C_nH_{2n} + NO_2 + C_nH_{2n} - NO_2$.

In 1876 Kühne* published a paper on the digestion of albumin which has attracted considerable attention, the views expressed therein being generally accepted, and even now appearing in one of the more forward text-books of the science. Taking advantage of Schützenberger's work, he has arrived at a clear conception of the breaking up of albumin by the digestive fluids, and brought into line many scattered bodies which have hitherto stood by themselves without any apparent relationship to each other or to the original albumin. Thus the *a*, *b* and *c* peptones of Meissner, and the syntonin, parapeptone and dyspeptone, so variously described, are all accounted for, and their derivation and relationship clearly pointed out. Kühne considers the albumin molecule to contain two residues, one of which he calls the anti- the other the hemi-residue.

Now by the digestion of albumin with pancreatic juice, for example, the trypsin transforms the albumin completely into peptones which are not exactly alike; the anti-residue has given antipeptone while the hemi-residue has yielded hemipeptone, the two differing from each other in the fact that the antipeptone is not capable of further change, that is, trypsin or pepsin is not able to alter it further, while the hemipeptone is changed by the further digestive action of trypsin in toleucin, tyrosin, and from the recent experiments of Salomon and Chittenden into hypoxanthin and xanthin. Thus in the digestion of albumin there are two stages: in the first the albumin is converted into peptones; in the second, one-half of the peptones (hemipeptone) is further decomposed while the antipeptone remains unchanged. Following is Kühne's scheme of the decomposition of albumin by digestion:



* Verhandl. Naturhist. Med. Verins. Heidel. 1876.

Before the anti- or hemipeptones are formed, however, intermediate products appear which correspond to bodies already known; thus as preliminary to antipeptone, antialbumose is formed, which has long been known as syntonin, while as preliminary to hemipeptone we have hemialbumose, which has long been described by Meissner as *a* peptone. These intermediate products are arranged by Kühne in schedule form as follows:

Albumin.	
Anti-group	Hemi-group
Antialbumid (Hemiprotein)	
Antialbumat (Parapeptone)	
Antialbumose (Syntonin)	Hemialbumose (*A*-peptone)
Antipeptone	Hemipeptone

Schützenberger's insoluble hemiprotein, which Kühne calls antialbumid, is wholly insoluble in gastric juice, but is soluble in dilute soda solution, and in that condition is readily digested by trypsin. At the end of the digestion nothing is precipitated by neutralization, and no trace of leucin or tyrosin can be detected, only antipeptone. Kühne's antialbumat has long been known as Meissner's parapeptone, a body formed by digestion in the presence of an insufficient quantity of pepsin, and which probably is never a product of normal digestion.

The antialbumat, as Meissner has previously said of parapeptone, is soluble in gastric juice, but not digestible, while by trypsin it is readily digested with formation of antipeptone. By the long continued action of dilute acid on the antialbumat it is converted into the much more difficultly soluble antialbumid, which has previously been described by Meissner as dyspeptone, a body totally insoluble in acid of the strength of the gastric juice, but readily dissolved by dilute alkali, and like its fellows converted into antipeptone by trypsin.

Antialbumose or syntonin is found in the so-called neutralization precipitate, obtained from digestive fluids of good strength, but when the digestion has not been completed. In solubility and in reactions antialbumose does not differ from syntonin, neither as regards its digestibility in gastric juice, but on testing the peptones formed towards trypsin it is found that they are unalterable; in other words they are antipeptones.

The typical substance of the hemi-group, and which Kühne calls hemialbumose, corresponding to Schützenberger's hemialbumin, can be formed, as already described, by the decomposition of albumin by acid; it is also found normally in an incompleted pepsin digestion. Thus according to Schützenberger's method of decomposition, after the removal of the hemiprotein a clear fluid is obtained which, on neutralization with ammonia, fails to give any precipitate whatever. By evaporating this fluid and extracting the residue with

alcohol, which takes up considerable leucin, a residue remains which dissolves readily in a small quantity of hot water, and on cooling separates out again as a snow-white powder. This is the substance which Kühne calls hemialbumose, a substance which can always be obtained with a considerable degree of purity, but only in small quantity as it is readily decomposable. Hemialbumose is difficultly soluble in cold water, easily in hot water; it is precipitated in the cold by nitric acid, dissolving in slight excess with a deep yellow color. Acetic acid and potassium ferrocyanide give a heavy precipitate, while alkali and cupric sulphate give an intense red color. In 10 per cent. salt solution hemialbumose is soluble, and forms when in sufficient quantity a jelly-like mass which, when laid in water, appears white and opaque. In dilute alkalis and acids hemialbumose is readily soluble, and is precipitated by neutralization only so far as the quantity of salt formed will allow. By pepsin and by trypsin hemialbumose is very readily changed; the body formed being in both cases hemipeptone, which, by trypsin digestion, is further decomposed into leucin, tyrosin, and other decomposition products. Hemialbumose is without doubt the same body described by Meissner as *a*-peptone, and everything tends to show that in the case of a weak digestive mixture it would not fail to be present, for Kühne says that when a digestion is broken into early large quantities can be detected, while traces have been found even after sixteen hours' digestion with a large excess of pepsin and a large quantity of acid.

Thus in the digestion of albuminous matter it is plain that by the first step in digestion the albumin molecule is resolved into its two parts, the gastric juice then readily changing the hemialbumose into hemipeptone, while the anti-group appears less susceptible to the action of pepsin, only a small portion of this group being changed into antipeptone, while the larger part, under the influence of the dilute acid, appears to be converted into partially insoluble products; but on reaching the intestinal canal these insoluble bodies, under the influence of the alkaline solution of trypsin, pass readily into solution and are digested with formation of antipeptone, which is readily absorbed, while the hemipeptone is further changed into crystalline decomposition-products.

R. H. CHITTENDEN.

DR. JUL. POST. GRUNDRISS DER CHEMISCHEN TECHNOLOGIE. Berlin. Oppenheim. 1877 and 1879.

This work, as the author states in his preface, is intended to serve as a text-book for industrial chemistry comparable in aim and scope with the manual of Wöhler and Fittig for general chemistry, to be short, but as far as possible complete, and adapted for use in teaching.

The first half, published in 1877, discussed the fabrication of crude products, the materials for further treatment, though sometimes directly used; the second half, which appeared in the latter part of last year, is occupied with the fabrication of final products, such as pass into immediate consumption. The arrangement is based, not mainly upon the chemical relationship or analogy of application of the individual products turned out, but rather upon the general character and grouping of the crude materials obtained from natural sources and of the industries based upon these, the history of each industry being worked out to its principal and subsidiary results. While this plan is a sound one on which to base a treatise upon chemical technology, it renders the discussion of some parts of the subject rather complicated, and, in view of the various ways in which processes are often combined in different manufacturers' hands, it necessitates frequent partial repetition and many cross references. In some instances the arrangement involves defect of logical order, as in the case of coal tar, the distillation and utilization of which are taken up before an account has been given of its production in connection with the manufacture of illuminating gas.

A good idea, but ill carried out, is that of a preliminary chapter on the general methods of chemical work on the great scale, such as crushing, grinding, solution, precipitation, filtration, distillation, the purification of water for technical use, the production and application of heat and cold, &c. This chapter is, however, very incomplete. For example, neither here nor in connection with the subject of the working of metallic ores, is any satisfactory reference even made to the means of subdividing and pulverizing hard materials, and such generally important processes as fractional precipitation and fractional distillation are left undiscussed.

Throughout the work the most prominent fault is the meagreness of detail with which mechanical appliances and methods are treated, while these, upon which the success or failure of a process often depends, cannot rationally be ignored or separated from the chemistry of the subject. In the explanation of the mechanical features of most great industries good figures are indispensable; those in this work vary in style of engraving, are often on too small a scale to be intelligible—*e. g.* the figures of coal-gas and sulphuric acid works—and their number is quite too small for adequate illustration of the subject. On the other hand, useful tabular schemes are often introduced to show at a glance the various stages and results of the more complicated manufactures, as of the dry distillation of lignite for paraffine, the treatment of copper ores, the treatment of mixed argentiferous ores at Freiberg, the English mode of working burnt pyrites, the crystallization of the potash salts of the Stassfurt beds, the manufacture of aniline red by means of arsenic acid, &c. Some other tables of this kind might have been added with advantage, as in illustration of the distillation of petroleum.

Some few inaccuracies of statement have been allowed to creep in; thus we are told that gold is "next to platinum," the most malleable of metals, but in general the author well supports the German reputation for care in avoiding manifest errors of pen or press. The book is largely characterized by over condensation of abundant and well collected material. There are some instances of want of due proportion in the treatment of different subjects, such as the devotion of 12 pages to gelatine and glue, while but 10 pages are allotted to the whole manufacture of sulphuric acid. Some of the industries based upon organic material—*e. g.* the treatment of fats, fermentation, and the manufacture of organic dye-stuffs of artificial origin—are discussed better and with more fulness than in the older text-books.

On the whole, the work is to be viewed as a syllabus or set of condensed notes, such as might be taken by an intelligent student during a course of lectures on chemical technology, rather than as a self-explanatory handbook for independent study or general reading. Thus considered it has real merit, and to the moderately advanced student who has access to other sources of information, or to the intelligent manufacturer who wishes for a general survey merely of other chemical industries than his own, it will undoubtedly be useful. J. W. M.

J. Girardin. Leçons de Chimie Élémentaire appliquée aux Arts Industriels. 6ième édition. 5 Vol.; augmentée d'un Supplément. Paris. G. Masson. 1880.

This work differs greatly in its plan from that of Dr. Post, reviewed above, though treating of the same subject, and will suit the purposes of a different class of readers, or in the same hands each may in large measure serve as the complement of the other. M. Girardin, director of the *École Supérieure des Sciences* of Rouen, has aimed at the production of a treatise, less condensed than that of Post, but still of moderate size, and, considering the form in which it is sent out from the press, very moderate in price; adapted to general reading on the part of those who have no special knowledge of the subject previously, and particularly suited for the use of the class of intelligent *ouvriers* of whom France may well be proud, and upon whose continued existence and improvement depends so largely her material prosperity.

The general arrangement of the work is based upon a gradually developed sketch of the simpler principles of chemistry, and of descriptive chemistry; the first volume being devoted to the non-metallic elements, the second to the metals, the third and fourth to vegetable and the fifth to animal materials; while the supplement contains in the same order the results of the more recent discoveries and improvements, along with that most useful feature, often wanting in French books, a copious index to the whole.

In each chapter the substances prominently, almost exclusively,

described are those utilized on an industrial scale, and the usual method for the production of each substance, its character and uses, are explained with much of the lucidity and elegance of style which distinguish French scientific writers.

While the author, bearing in mind for whom he writes, has avoided as far as possible the use of symbols and much reference to the atomic constitution of bodies, especially in the earlier portions of the book, thus marring it for the scientific student, it is a pity that, so far as such matters have been touched upon at all, the atomic weights and unitary formulæ now so generally in use have not been employed instead of the old equivalents (C=6, O=8, etc.,) and the binary mode of representing salts and the like.

On the side of the detailed industrial treatment of each substance, moreover, for the greater part only a general description is given of the most usual procedure; variations of method, even when important, being but briefly referred to or not mentioned at all, and in some instances, which would have admitted of the incorporation of notable improvements with the general description—*e. g.* the Glover tower in the manufacture of sulphuric acid—such improvements have been passed over in silence.

A minor but specially interesting feature of the book is the fulness of the historical notices prefixed to most of the accounts of chemical processes and their products, including often biographical details in reference to the men who have been conspicuous in the development of each industry. Many little-known facts are to be found recorded in these sketches, particularly in regard to the history of industrial progress in France—as, for example, notice of the part played by the English Jacobin, Holker, after his flight to France, in the development of the sulphuric acid manufacture of the 18th century in his adopted country; of the relation of his grandson, Jean Holker, to the same industry in the days of the first Empire; of the success of Delessert, under Chaptal's auspices, in the production on a commercial scale of beet-root sugar, etc.

More than fourteen hundred good, clear woodcuts, many of them designed with much taste, serve to illustrate the book, and among these some have been chosen with an eye to the picturesque local surroundings of a manufacture which adds much to the suggestiveness of the description. Thus, under sugar, we have a view of the interior of an old-time Martinique sugar-mill with vertical wooden cylinders for crushing the cane, and under natural dye-stuffs two views of an indigo factory on the Coromandel coast. There are also inserted a number of well-selected specimens of dyed fabrics in silk and other goods and of printed cotton cloth.

The work is one of popular character, but it is essentially a very good example of what a popular scientific book should be. A very fair course of elementary reading for a student of industrial chemistry might consist of the treatises of Girardin, v. Wagner, and Post, taken up in the order in which they are here named.

J. W. M.

RECENT PUBLICATIONS RELATING TO CHEMISTRY.

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LEGG, J. W. A Guide to the Examination of the Urine. 5th Edition. London: Lewis. 2s. 6d.

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LUFF, A. P. An Introduction to the Study of Chemistry, specially designed for Medical and Pharmaceutical Students. London: Churchill. 2s. 6d.

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III.—French.

MENNIER, S. Traité pratique de chimie et de géologie agricoles. Paris: Rothschild. 3fr. 50.

RITTER. Cours de Chimie. Leçons faites à la faculté de médecine de Nancy. Recueillies par M. L. Garnier. Deuxième partie, chimie toxicologique. Paris et Nancy: Berger-Levrault.

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